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1-Naphthyl derivatives of class ArFbX<sub>3</sub>.

V.I.Lodochnikova, B.M.Fanov and K.A.Kocheshkov (State Med.Inst., Sverdlovsk). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1484-6.

To 4.9 g. Pb(OAc)<sub>4</sub> in 50 ml. CHCl<sub>3</sub> acidified with little AcOH was added 5 g. (1-C<sub>10</sub>H<sub>7</sub>)<sub>2</sub>Hg; after 1.5 hrs. the mixture was treated at 0° with 1 equiv. HCl in 4.9 ml. HCl yielding 87% 1-C<sub>10</sub>H<sub>7</sub>HgCl, and evapn. of the filtrate gave 55.1% 1-C<sub>10</sub>H<sub>7</sub>Pb(OAc)<sub>3</sub><sup>(I)</sup>, m. 168-9° (from EtOAc + AcOH). Similarly was prepd. 46% (iso-PrCO<sub>2</sub>)<sub>3</sub>PbC<sub>10</sub>H<sub>7</sub>-1<sup>(II)</sup>, m. 99.5-101° (from hexane-isopentane). The triacetate with MeOH-aq. NH<sub>4</sub>OH overnight gave 62.6% 1-naphthylplumbonic acid, yellow amorphous solid, which ignites in a flame and is nearly insol. in 50% KOH or concd. HCl; with AcOH it yields I and with iso-PrCO<sub>2</sub>H it yields II. I treated with BzOH in C<sub>6</sub>H<sub>6</sub>-hexane gave 40.5% 1-C<sub>10</sub>H<sub>7</sub>Pb(OBz)<sub>3</sub>, m. 173-4° (from hexane)

Synthesis of aromatic compounds of antimony. IX. Preparation of aromatic antimony compounds by means of antimony pentachloride and phenylhydrazine. A.B. Bruker. Zhur. Obshchei Khim. 27, 2700-4 (1957). Cf. this j. 27, 2593 (1957). To 240 ml.  $H_2O$  and 120 ml. concd. HCl was gradually added 30 g.  $SbCl_5$ , followed by 3.5 g.  $FeCl_3$  and ~~after 20 min. by 0.3 g.  $CuCl_2$  in 10 ml. 1:2 HCl.~~ 29 g.  $PhNHNH_2 \cdot HCl$  followed after 20 min. by 0.3 g.  $CuCl_2$  in 10 ml. 1:2 HCl. After 50 hrs. of stirring over 8 days, the ppt. was sepd. and washed with 1:2 HCl, EtOH and  $Et_2O$ , yielding 40 g. yellowish  $PhN_2Cl \cdot PhSbCl_2^{(I)}$ , which evolves  $N_2$  in soln. with  $Me_2CO$ ; boiling with aq. HCl yields  $Ph_2SbCl_3 \cdot H_2O$ , dec.  $173^\circ$ , in 45% yield. I (5 g.) in warm 1:2 HCl (125 ml.) was treated with 15 ml. EtOH and filtered, then treated with 1-2 crystals ~~of~~ KI and treated with  $SO_2$  40-60 min. yielding on cooling 77%  $Ph_2SbCl_3$ , m. 69-70% concn. of the mother liquor yields addnl. amount of product).  $PhN_2Cl$  from 32.5 g.  $PhNH_2$  was added under the surface of soln. of 74.9 g.  $SbCl_5$ , 38 g.  $PhNHNH_2 \cdot HCl$ , 2 g.  $CuCl_2$  and 750 ml. 5.8% HCl over 4 hrs. at  $-5^\circ$ ; after 2 hrs. the ppt. was sepd. and washed as above yielding 70.3%  $PhN_2Cl \cdot PhSbCl_2$ , which heated in aq. HCl yields I. To  $PhN_2Cl$  soln. from 10 g.  $PhNH_2$  was added at  $0^\circ$  30 g.  $SbCl_5$ , yielding a ppt. of 97%  $PhN_2Cl \cdot SbCl_5^{(II)}$ , dec.  $85^\circ$ , which gives a coupling product with 2-naphthol. To 120 ml. HCl and 240 ml.  $H_2O$  was added ~~44 g. II~~ and 15 g.  $PhNHNH_2 \cdot HCl$  and 3 g.  $FeCl_3$ , followed after 20 min. by 0.3 g.  $CuCl_2$  in 10 ml. dil. HCl, yielding after 183 hrs. 16%  $Ph_2SbCl_3 \cdot H_2O$ , after sepn. of the ppt. and decomposing it with hot 1:2 HCl. To 360 ml. 1:2 HCl was added 30 g.  $SbCl_5$ , 22 g.  $PhNHNH_2$  and 3 g.  $FeCl_3$ , followed in 20 min. ~~by~~ 0.3 g.  $CuCl_2$  in 10 ml. 1:2 HCl yielding after 33 days 22 g.  $PhNHNH_2 \cdot HCl$  as a ppt., and the filtrate yielding 9 g. inorganic Sb; no organic derivs. of Sb were formed. To 360 ml. 1:2 HCl was added 44 g. II, 15 g.  $PhNHNH_2 \cdot HCl$  and 3 g.  $FeCl_3$ , followed in 20 min. by 0.3 g.  $CuCl_2$  in 10 ml. 1:2 HCl, yielding in 20 hrs. 24 g. ppt. which treated with hot 1:2 HCl gave 15%  $Ph_2SbCl_3 \cdot H_2O$ . No organic derivs. were formed from 22 g.  $PhNHNH_2$ , 30 g.  $SbCl_5$  and 360 ml. 1:2 HCl in 47 days. II and  $PhNHNH_2 \cdot HCl$  failed to react alone without added catalysts.

**Synthesis of aromatic compounds of antimony. VIII. Preparation of p-tolyl- and  $\beta$ -naphthylantimony compounds.**

A.B. Bruker. Zhur. Obshchei Khim. 27, 2593-8 (1957). Cf. 27, 2220 (1957) and 27, 2223 (1957).

To a soln. of 28.5 g.  $\text{SbCl}_3$  and 21.2 g.  $\text{CuCl}_2$  was added 20 g.  $p\text{-MeC}_6\text{H}_4\text{NH-NH}_2\cdot\text{HCl}$  and after 12 hrs. the ppt. was washed with dil.  $\text{HCl}$ ,  $\text{EtOH}$  and  $\text{Et}_2\text{O}$  yielding 40% brown  $(p\text{-MeC}_6\text{H}_4\text{N}_2\text{Cl})_2\cdot p\text{-MeC}_6\text{H}_4\text{SbCl}_2^{(\text{I})}$ , dec.  $115^\circ$ , which refluxed with 1:2  $\text{HCl}$  evolves  $\text{N}_2$  and forms mainly  $p\text{-MeC}_6\text{H}_4\text{SbCl}_4$ , and some  $(p\text{-MeC}_6\text{H}_4)_2\text{SbCl}_3$ , m.  $155^\circ$ . The filtrate treated with satd.  $\text{NH}_4\text{Cl}$  in concd.  $\text{HCl}$  gave 3 g. yellow  $p\text{-MeC}_6\text{H}_4\text{SbCl}_4\cdot\text{NH}_4\text{Cl}^{(\text{II})}$ , does not m.  $200^\circ$ , which treated with  $\text{H}_2\text{O}$  gave p-tolylstibinic acid, does not m.  $200^\circ$ , which rubbed with  $\text{HCl-EtOH}$  and some  $\text{H}_2\text{O}$ , filtered and treated with a little  $\text{KI}$  and satd. with  $\text{SO}_2$  at  $0^\circ$  gave  $p\text{-MeC}_6\text{H}_4\text{SbCl}_2$ , m.  $92-3^\circ$ , which forms readily from I on treatment with 1:2  $\text{HCl}$ , a little  $\text{KI}$  and satn. with  $\text{SO}_2$ . The oil formed in decompn. of I yields after treatment with aq.  $\text{Me}_2\text{CO}$  some p,p'-ditolyl. Similarly,  $p\text{-MeC}_6\text{H}_4\text{N}_2\text{Cl}\cdot\text{SbCl}_3$  and  $p\text{-MeC}_6\text{H}_4\text{NHNH}_2\cdot\text{HCl}$  with  $\text{CuCl}_2$  gave 60%  $p\text{-MeC}_6\text{H}_4\text{N}_2\text{Cl}\cdot p\text{-MeC}_6\text{H}_4\text{SbCl}_2$ , dec.  $115^\circ$ , which with 1:2  $\text{HCl}$  gave  $(p\text{-MeC}_6\text{H}_4)_2\text{SbCl}_3$ , m.  $155^\circ$ , while  $\text{NH}_4\text{Cl}$  yields II identical with the above described. To 100 ml. concd.  $\text{HCl}$ , 200 ml.  $\text{H}_2\text{O}$ , 28.5 g.  $\text{SbCl}_3$  and 22 g.  $\text{CuCl}_2$  was added 24.8 g.  $2\text{-C}_{10}\text{H}_7\text{NHNH}_2\cdot\text{HCl}$ , yielding as above 49-51%  $(2\text{-C}_{10}\text{H}_7\text{N}_2\text{Cl})_2\cdot 2\text{-C}_{10}\text{H}_7\text{SbCl}_2^{(\text{III})}$ , dec.  $98^\circ$ , which with  $\text{NH}_4\text{Cl}$  in 1:2  $\text{HCl}$  gave  $2\text{-C}_{10}\text{H}_7\text{SbCl}_4\cdot\text{NH}_4\text{Cl}$ , does not m.  $200^\circ$ , which with  $\text{H}_2\text{O}$  gave 90% 2-naphthylstibinic acid, does not m.  $200^\circ$ , which after treatment as above gave 85%  $2\text{-C}_{10}\text{H}_7\text{SbCl}_2$ , m.  $102^\circ$ , also formed directly from the double salt after reduction with  $\text{SO}_2$  as above. The dichloride with aq. alc.  $\text{NH}_4\text{OH}$  gave 88% 2-naphthylstibine oxide, dec.  $160^\circ$  [the oil from the decompn. of the double salt gave 2,2'-dinaphthyl. Concd.  $\text{HCl}$  (100 ml.), 200 ml.  $\text{H}_2\text{O}$ , 1 g.  $\text{CuCl}_2$ , 2 g.  $\text{FeCl}_3$ , 52.3 g.  $2\text{-C}_{10}\text{H}_7\text{N}_2\text{Cl}\cdot\text{SbCl}_3$  and 24.8 g.  $2\text{-C}_{10}\text{H}_7\text{NHNH}_2\cdot\text{HCl}$  in 40 hrs. gave 54% III.

Reaction of arylazocarboxylic salts with cis- and trans- $\beta$ -chlorovinylmercuric chlorides.

O.A.Reutov and E.M.Fedneva (State Univ., Moscow). Zhur.Obshchei Khim.27,2506-8(1957).

Reaction of 35.7 g. trans-CHCl:CHHgCl with 29.5 g. PhN<sub>2</sub>CO<sub>2</sub>K in dry Me<sub>2</sub>CO rapidly yields a ppt. of KCl, KHCO<sub>3</sub> and Hg and forms 18.5% PhHgCl and 12% trans-PhCH:CHCl. Cis-CHCl:CHHgCl similarly gave 12% PhCH:CHCl, b<sub>18</sub>60-4°, ~~n<sub>D</sub><sup>15</sup>1.5802, d<sub>18</sub>1.1623~~ n<sub>D</sub><sup>15</sup>1.5763, d<sub>15</sub>1.1623, which is probably the cis-isomer.

Reaction of trans-CHCl:CHHgCl with p-MeC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>K similarly gave 12% p-MeC<sub>6</sub>H<sub>4</sub>-CH:CHCl, b<sub>14</sub>99-101°, n<sub>D</sub><sup>27</sup>1.5660.

Reaction of  $\alpha$ -alkoxyacrylonitriles with mercuric acetate. Preparation of esters of monomercurated acetic acid.

I.F. Lutsonko, L.F. Badenkova and V.I. Foss. Zhur. Obshehei Khim. 27, 3261-4 (1957)

To 135.7 g.  $\text{Cu}(\text{CN})_2$  in 375 ml. abs.  $\text{Et}_2\text{O}$  was added with cooling 373.5 g.  $\text{BrCH}_2\text{ClBrOPr}$  and after 1 hr. at room temp. and 2 hrs. at reflux the mixture gave 55.8%  $\text{BrCH}_2\text{CH}(\text{OPr})\text{CN}$ ,  $b_7.5$  86-8°. Similarly was prepd. 38%  $\text{BrCH}_2\text{CH}(\text{OBu})\text{CN}$ ,  $b_8$  90-100°. Both nitriles decompose on standing and during distn. and must be used immediately. Treatment of these with  $\text{Et}_2\text{NH}$  in  $\text{Et}_2\text{O}$  gave 73%  $\text{CH}_2=\text{C}(\text{OPr})\text{CN}$ ,  $b_{20}$  59.5°,  $n_D^{20}$  1.42305,  $d_{20}^{20}$  0.8996, and 55%  $\text{CH}_2=\text{C}(\text{OBu})\text{CN}$ ,  $b_{10}$  63.2°, 1.4279, 0.8924, resp. The former with 0.2 moles  $\text{Hg}(\text{OAc})_2$  in  $\text{H}_2\text{O}$  rapidly gave 95%  $\text{AcOHgCH}_2\text{CO}_2\text{Pr}$ , m. 109-11°, which with aq.  $\text{KCl}$  gave  $\text{ClHgCH}_2\text{CO}_2\text{Pr}$ , 62%, m. 59-62°, while  $\text{KBr}$  similarly gave  $\text{BrHgCH}_2\text{CO}_2\text{Pr}$ , 73%, m. 42-3°. Similarly were obtained:  $\text{AcOHgCH}_2\text{CO}_2\text{Me}$ , m. 135-6°;  $\text{AcOHgCH}_2\text{CO}_2\text{Et}$ , 89%, m. 116°;  $\text{ClHgCH}_2\text{CO}_2\text{Et}$ , 92%, m. 66°;  $\text{BrHgCH}_2\text{CO}_2\text{Et}$ , 54%, m. 43-5°;  $\text{AcOHgCH}_2\text{CO}_2\text{Bu}$ , 90%, m. 89-91°;  $\text{BrHgCH}_2\text{CO}_2\text{Bu}$ , 75%, m. 30°.

# Synthesis and properties of trichloromethyl and $\gamma,\gamma$ -dichloroallyl compounds of mercury.

A.N. Nemanov, R.Kh. Froidlina and P.K. Volichko (Inst. Hetero-org. Compounds, Acad. Sci., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1958, 40-6.

Refluxing  $\text{CCl}_3\text{CH}=\text{CH}_2$  with NaI in  $\text{Me}_2\text{CO}$  1.5 hrs. gave after aq. treatment 34% 3-iodo-1,1-dichloro-1-propene,  $b_p 63^\circ$ ,  $n_D^{20} 1.6020$ ,  $d_{20} 2.0320$ , which is rather unstable. This and Hg illuminated with a mercury lamp 0.5 hr. gave 67%  $\text{CCl}_2:\text{CHCH}_2\text{HgI}$ ,  $m. 46^\circ$  (from  $\text{CHCl}_3$ ). This with  $\text{Ag}_2\text{O}$  in hot  $\text{EtOH}$ , refluxed 20 min., filtered and treated with aq. NaCl and acidified with HCl, to phenolphthalein, gave after 12 hrs. 71.5%  $\text{CCl}_2:\text{CHCH}_2\text{HgCl}$ ,  $m. 100^\circ$  (from  $\text{CHCl}_3$ ); this failed to form a pyridine complex. Similarly was prepd. 70%  $\text{CCl}_2:\text{CHCH}_2\text{HgBr}$ ,  $m. 93-4.5^\circ$ . Heating 7.5 g.  $\text{CCl}_3\text{Br}$ , 80 g. Hg and 0.01 g.  $(\text{Me}_2\text{C}(\text{CN})\text{N})_2$  under ultraviolet lamp 3 hrs. at  $80^\circ$  gave after extrn. with hot  $\text{Me}_2\text{CO}$  41%  $\text{CCl}_3\text{HgBr}$ ,  $m. 165^\circ$  (from  $\text{CHCl}_3$ ); this with pyridine in  $\text{C}_6\text{H}_6$  gave a yellow equimolar complex,  $\text{dec. } 87^\circ$  (from  $\text{C}_6\text{H}_6$ ). I and  $\text{Ag}_2\text{O}$  in  $\text{EtOH}$  gave 75%  $\text{CCl}_3\text{HgOH}$ ,  $\text{dec. } 175^\circ$  (from  $\text{CHCl}_3$ ), which with 2N HCl gave 70%  $\text{CCl}_3\text{HgCl}$ ,  $\text{dec. } 173^\circ$ . Similarly was obtained 56%  $\text{CCl}_3\text{HgI}$ ,  $\text{dec. } 116-7^\circ$ , also formed from  $\text{CCl}_3\text{I}$  and Hg. Treatment of  $\text{CCl}_3\text{HgBr}$  with 0.5 mole  $\text{Ph}_2\text{SnCl}_2$  in  $\text{EtOH}$  in the presence of NaOH gave 23%  $\text{CCl}_3\text{HgPh}$ ,  $m. 126-7.5^\circ$  (from  $\text{EtOH}$ ), which with  $\text{MeOH-HCl}$  gave 84%  $\text{PhHgCl}$ ; larger amount of NaOH in the above reaction gave  $\text{Ph}_2\text{Hg}$ .  $\text{PhHgOH}$  in  $\text{EtOH}$  was treated with aq.  $\text{CCl}_3\text{CO}_2\text{H}$  yielding 78%  $\text{CCl}_3\text{CO}_2\text{HgPh}$ ,  $\text{dec. } 238-40^\circ$  (from aq.  $\text{MeOH}$ ). This in  $\text{MeOH}$  under ultraviolet radiation for 8 hrs. gave 94%  $\text{PhHgCl}$ .  $\text{CCl}_3\text{HgCl}$  and dry  $\text{NH}_3$  in  $\text{CHCl}_3$  gave 95.5%  $\text{ClHgNH}_2$ . Passage of  $\text{H}_2\text{S}$  into alc. soln. of  $\text{CCl}_3\text{HgBr}$  0.5 hr. gave 98.7%  $\text{HgS}$ .

Isotope exchange of some organomercury salts with metallic mercury labelled with Hg-203.

O.A. Roudov and U Yen-Tsai (M.V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 117, 1003-6 (1957).

At room temp. rapid and substantially complete isotope exchange takes place between Hg<sup>203</sup> and Hg of: o-ketocyclohexylmercuric bromide, PhCH(HgBr)-CO<sub>2</sub>Et, PhCH(HgBr)CO<sub>2</sub>C<sub>10</sub>H<sub>19</sub>; the reaction is much slower and restricted with 3-bromomercuri-3-benzylcamphor and 3-bromomercuricamphor, while no exchange was observed with 1-chloromercuricamphenylone, 2-bromomercuricamphane and BuHgBr. Owing to mild conditions, the reaction is believed to be purely molecular-atomic in nature and probably occurs without formation of free radicals.



*organomercury*

Reaction of isotope exchange of symmetric organomercury compounds of the aromatic series with metallic mercury labelled with Hg-203.

O.A.Reutov and G.M.Ostapchuk (M.V.Lomonosov State Univ., Moscow). Doklady Akad.Nauk S.S.S.R.117, 286-8(1957).

Isotope equil. ~~in xylene~~ at  $140^{\circ}$  is attained in xylene for Hg and  $\text{Ph}_2\text{Hg}$  in 30 min., but for dioxane soln. this requires 2.75 hrs. In dioxane at  $60^{\circ}$  the equil. for  $(p\text{-MeOC}_6\text{H}_4)_2\text{Hg}$  and Hg is attained in 1 hr. while in  $\text{C}_6\text{H}_6$  at  $20^{\circ}$  this is reached in 16 hrs. Exchange of Hg is accelerated by elevated temp. and excess metallic Hg. The rate of isotope exchange rises in diaryl derive. of Hg with the following series of groups:  $\text{O}_2\text{N}$ , Cl, H, Me, OMe. Since the conditions are mild, it is suggested that the exchange occurs not by radical route but by direct molecular-atomic interaction. Since the mixture of equilibrated Hg and  $\text{PhHgC}_6\text{H}_4\text{NO}_2\text{-p}$  does not contain any other products, the above argument appears to be validated.

*in general*  
Thermographic study of the process of dehydration of orthoboric acid. V.V.Urusov (Ya.V.Samoilov Res.Inst. Fertilizers and Insectofungicides, Moscow). Doklady Akad.Nauk S.S.S.R. 116, 97-100(1957).

Thermograms obtained from  $H_3BO_3$  at various levels of external pressure are reproduced. At 740-65 mm pressure the dehydration is a 2-step process with intermediate formation of  $HBO_2$  at  $101^\circ$  to  $149^\circ$  depending on external pressure; the 2nd effect at  $176^\circ$  is that of melting of  $HBO_2$  at 740 mm.; at lower pressure this effect corresponds to the course of dehydration of  $HBO_2$  with formation of a soln. at  $147^\circ$  to  $175^\circ$ , depending on the pressure. The solns. formed in the 2nd effect evaporate without formation of a solid phase and yield  $B_2O_3$ . Dehydration of  $H_3BO_3$  at 15-50 mm yields a 3-step process: at  $83^\circ$  to  $96^\circ$  the formation of  $HBO_2$  occurs, at  $112^\circ$  to  $143^\circ$   $HBO_2$  dissociates either into an intermediate hydrate or a solid soln. and steam, and the 3rd effect at  $144-50^\circ$  results from dissocn. of the hydrate or the solid soln. to steam and  $B_2O_3$ . The dissocn. pressure in the 1st step is below the literature values for the equil.pressure (cf. Kracek et al. Am.J.Sci.35A,143(1938), and Tazaki, J.Sci.Hiroshima Univ.,Ser.A.10,37, 55, 63, 109, 113(1940)). The 2nd hydrate contains 80.4-82.2%  $B_2O_3$  and appears to be a new hydrate. At 15 mm pressure the dehydration may appear as a 3-step process in part and as 1-step process in part, which appears in the form of 5 singular points on the thermogram. At 10 mm. the 1-step process is apparent, the acid dissociating directly to amorphous  $B_2O_3$  and steam at  $96-8^\circ$ .

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Reactivity of allyl derivatives of tin.

M.M.Koton and T.M.Kiseleva (Inst.High Polymers, Acad.Sci.,Leningrad). Zhur. Obshehei Khim.27, 2553-8(1957).

Heating  $\text{Sn}(\text{CH}_2\text{CH}:\text{CH}_2)_4$  in ampul at  $170^\circ$  gave  $\text{CH}_2:\text{CHCH}_2\text{SnO}_2\text{H}$ ; in 48 hrs. the products are Sn,  $\text{SnO}_2$  and diallyl; if the heating is done with isobutyroazonitrile at  $160^\circ$  there is formed an infusible solid containing 55.1% Sn. No change was observed in  $\text{Ph}_2\text{Sn}(\text{CH}_2\text{CH}:\text{CH}_2)_2$  in ampul at  $160^\circ$ , but over  $160^\circ$   $\text{Ph}_4\text{Sn}$  is formed.  $\text{Ph}_3\text{SnCH}_2\text{CH}:\text{CH}_2$  at  $170^\circ$  does not change. At room temp.  $\text{Sn}(\text{CH}_2\text{CH}:\text{CH}_2)_4$  and alc.HCl yield propylene and  $\text{SnO}_2$ ;  $\text{Ph}_2\text{Sn}(\text{CH}_2\text{CH}:\text{CH}_2)_2$  with alc.HCl yields  $\text{C}_6\text{H}_6$  and propylene and  $\text{Ph}_2\text{SnO}$ , while  $\text{Ph}_3\text{SnCH}_2\text{CH}:\text{CH}_2$  and alc.HCl yield propylene,  $\text{C}_6\text{H}_6$ ,  $\text{SnO}_2$ .  $\text{Ph}_3\text{SiCH}_2\text{CH}:\text{CH}_2$  and  $\text{I}_2$  in hot xylene gave  $\text{Ph}_3\text{SnI}$ , m. 115-7°.  $\text{Sn}(\text{CH}_2\text{CH}:\text{CH}_2)_4$  and  $\text{HCO}_2\text{H}$  gave  $(\text{HCO}_2)\text{-Sn}(\text{OH})_3$ , infusible solid;  $\text{Ph}_2\text{Sn}(\text{CH}_2\text{CH}:\text{CH}_2)_2$  and  $\text{HCO}_2\text{H}$  in ampul at  $50^\circ$  gave  $\text{C}_6\text{H}_6$ , propylene and  $\text{HCO}_2\text{Sn}(\text{OH})_3$ ;  $\text{Ph}_3\text{SnCH}_2\text{CH}:\text{CH}_2$  reacts with  $\text{HCO}_2\text{H}$  at  $90^\circ$  yielding propylene,  $\text{C}_6\text{H}_6$  and  $\text{HO}_2\text{CSn}(\text{OH})_3$ .  $\text{Sn}(\text{CH}_2\text{CH}:\text{CH}_2)_4$  and EtOH at  $130^\circ$  gave propylene and  $\text{SnO}_2$ . None of the allyl derivs. polymerized on heating alone or with isobutyroazonitrile and inhibited other monomers.

Complex compounds of  $\text{SnCl}_4$ ,  $\text{SnBr}_4$  and  $\text{TiCl}_4$  with cineol.

I. Sumarokova and Yu. Nevskaya. Zhur. Obshchei Khim. 27, 3375-9(1957).

Cineol and  $\text{SnCl}_4$  in  $\text{C}_6\text{H}_6$  yield a complex  $\text{SnCl}_4 \cdot 2\text{C}_{10}\text{H}_{18}\text{O}$ , crystalline colorless solid which reddens in air and sublimes on heating. Similarly was formed  $\text{SnBr}_4 \cdot 2\text{C}_{10}\text{H}_{18}\text{O}$ , a crystalline solid which sublimes readily, and  $\text{TiCl}_4 \cdot 2\text{C}_{10}\text{H}_{18}\text{O}$ , orange-red solid.

# Reaction of direct substitution of hydrogen in organic compounds by thallium (thallilation).

V.P.Glushkova and K.A.Kocheshkov (L.Ya.Karpev Phys.Chem.Inst.). Invest. Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1186-92.

Cf. Doklady Akad.Nauk SSSR 103,615(1955).

Reaction of  $\text{Tl}(\text{O}_2\text{CCHMe}_2)_3$  (I) with excess  $\text{C}_6\text{H}_6$  gave 90%  $(\text{iso-PrCO}_2)_2\text{TlPh}$ , m.221°, sparingly sol. in warm  $\text{H}_2\text{O}$ ; with  $\text{HgCl}_2$  in refluxing  $\text{EtOH}$ , and addn. of  $\text{HCl}$  gave  $\text{PhHgCl}$ . Refluxing 2.35 g. I in 5 g.  $\text{MePh}$  1 hr. gave on evapn. 55% mixed isomers of  $(\text{iso-PrCO}_2)_2\text{TlC}_6\text{H}_4\text{Me}$ , m.185-6° (from xylene), which with  $\text{HgCl}_2$  gave mainly the p-isomer of  $\text{MeC}_6\text{H}_4\text{HgCl}$ . I and  $\text{C}_{10}\text{H}_8$  gave in 1 hr. at 115° 25%  $(\text{iso-PrCO}_2)_2\text{TlC}_{10}\text{H}_7$ , m.209°, which was the 2-isomer, as shown by conversion with  $\text{HgCl}_2$  to 2- $\text{C}_{10}\text{H}_7\text{HgCl}$ , m.270°. Reaction of I with  $\text{MeOPh}$  gave 44%  $(\text{iso-PrCO}_2)_2\text{TlC}_6\text{H}_4\text{OMe-p}$ , m.195°, which with  $\text{HgBr}_2$  in  $\text{MeOH}$ , followed by  $\text{HBr}$  gave pure p- $\text{MeOC}_6\text{H}_4\text{HgBr}$ , m.250-50.5°, which was checked with preps. from  $\text{R}_2\text{Hg}$  with  $\text{HgBr}_2$  or  $\text{H}_2\text{Hg}$  and  $(\text{iso-PrCO}_2)_2\text{Hg}$ .  $\text{EtOPh}$  and I gave 23% p- $\text{EtOC}_6\text{H}_4\text{Tl}(\text{O}_2\text{CCHMe}_2)_2$ , m.186.5°. o- $\text{C}_6\text{H}_4(\text{OMe})_2$  and I gave 75%  $(\text{MeO})_2\text{C}_6\text{H}_3\text{Tl}(\text{O}_2\text{CCHMe}_2)_2$ , m.188°, which with  $\text{I}_2\text{-CHCl}_3$  gave 1,2-dimethoxy-4-iodobenzene, m.34-5°, thus showing the site of entry of Tl in the 4-position. Similarly I and 1,3- $\text{C}_6\text{H}_4(\text{OMe})_2$  gave 73%  $(\text{MeO})_2\text{C}_6\text{H}_3\text{Tl}(\text{O}_2\text{CCHMe}_2)_2$ , m.147-8°; similarly p- $\text{C}_6\text{H}_4(\text{OMe})_2$  and I gave the isomer of the above, m.112-3°, in 43% yield. 1,3,5- $(\text{MeO})_3\text{C}_6\text{H}_3$  and I gave 87.5%  $(\text{MeO})_3\text{C}_6\text{H}_2\text{Tl}(\text{O}_2\text{CCHMe}_2)_2$ , m.117-8°. Thiophene heated 5 min. with I gave 88% 2- $\text{C}_4\text{H}_3\text{S.Tl}(\text{O}_2\text{CCHMe}_2)_2$ , m.215-6°. I and  $\text{AcPh}$  in 5 min. at 100° gave 45.5%  $\text{C}_{24}\text{H}_{34}\text{Tl}_2\text{O}_9$ , m.127-8°, which could not be recrystallized; the substance is evidently a tetraisobutyrate of dithalliumphenacylidene, which is not very stable in air; with aq.  $\text{Br}_2\text{-KBr}$  it gave  $\text{PhCOCHBr}_2$ , m.35°. I and excess dibenzofuran, gave dibenzofurylthallium diisobutyrate, m. 204-5° (cf. Gilman and Abbett, JACS 65, 122(1943)).

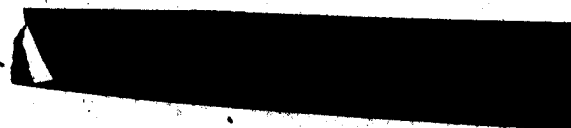
## organometallic

Reaction of diarylmercury with salts of trivalent thallium as a method of synthesis of compounds of class  $\text{ArTlX}_2$ .

V.P.Glushkova and K.A.Kocheshkov. Invest.Akad.Nauk S.S.S.R., Otdel.Khim. Nauk 1957, 1193-8.

In warm  $\text{CHCl}_3$   $(\text{iso-PrCO}_2)_3\text{Tl}$  and  $\text{Ph}_2\text{Hg}$  yield in 0.5 hr. 87.9%  $(\text{iso-PrCO}_2)_2\text{TlPh}$ , m.221-2°. Reaction of 2 moles  $\text{Ph}_2\text{Hg}$  with 1 mole  $(\text{iso-PrCO}_2)_3\text{Tl}$  in warm  $\text{CHCl}_3$  gave  $\text{iso-PrCO}_2\text{TlPh}_2$ , m.241° (from  $\text{ClCH}_2\text{CH}_2\text{Cl}$ ), which with  $\text{HgCl}_2$  yields  $\text{PhHgCl}$ . Similarly were obtained: 43.7% p- $\text{MeC}_6\text{H}_4\text{Tl}(\text{O}_2\text{CCHMe}_2)_2$ , m. 199.5-200°; 76% (p- $\text{MeC}_6\text{H}_4$ ) $_2\text{TlO}_2\text{CCHMe}_2$ , m.244-4.5° (decomp.);  $(\text{iso-PrCO}_2)_2\text{TlC}_{10}\text{H}_7\text{-1}$ , m.183-4°; 91%  $(\text{iso-PrCO}_2)_2\text{TlC}_{10}\text{H}_7\text{-2}$ , m.209-10°; 65%  $(\text{iso-PrCO}_2)_2\text{TlC}_6\text{H}_4\text{OMe-p}$ , m.196°; 66%  $(\text{iso-PrCO}_2)\text{Tl}(\text{C}_6\text{H}_4\text{OMe})_2\text{-p}$ , m.252°; & 67%

2-thionylthallium diisobutyrate, m. 216-7°; 73.5% p-ClC<sub>6</sub>H<sub>4</sub>Tl(O<sub>2</sub>CCMe<sub>2</sub>)<sub>2</sub>, m. 229° (decomp.). The latter (1 g.) in 25 ml. MeOH was treated with excess aq. NH<sub>4</sub>OH, kept 0.5 hr., dild. with H<sub>2</sub>O, filtered, the ppt. suspended in MeOH and treated with calcd. amount of alc. HCl, gave 0.65 g. p-ClC<sub>6</sub>H<sub>4</sub>TlCl<sub>2</sub>, m. 252°, which could not be recrystallized satisfactorily. Similarly were obtained: p-BrC<sub>6</sub>H<sub>4</sub>Tl(O<sub>2</sub>CCMe<sub>2</sub>)<sub>2</sub>, 50%, m. 219° (decomp.), and p-BrC<sub>6</sub>H<sub>4</sub>TlCl<sub>2</sub>, m. 261° (from StOAc).



Organomagnesium synthesis of vinyl derivatives of silicon, germanium and tin.

A.D.Petrov and V.F.Mironov (M.D.Zelinskii Inst.Org.Chem., Moscow). Izvest. Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1491-3.

To 11 g. Mg in 50 ml. tetrahydrofuran was added 0.5 g. EtBr followed by 30 g.  $\text{CH}_2\text{:CHBr}$  in 100 ml. tetrahydrofuran, and the resulting Grignard reagent was treated with 92 ml.  $\text{Et}_3\text{SnCl}$  with cooling. After 2 hrs. on a steam bath, followed by diln. with  $\text{Et}_2\text{O}$  and addn. of  $\text{H}_2\text{O}$  there was obtained 70 g.  $\text{Et}_3\text{SnCH:CH}_2$ , b.  $174-5^\circ$ ,  $n_D^{20}$  1.4780,  $d_{20}$  1.2133. Similarly the use of  $\text{EtSiHCl}_2$  gave 22%  $\text{EtSiH(CH:CH}_2)_2$ , b.  $93-4.5^\circ$ , 1.4305, 0.7539, while  $\text{Et}_2\text{GeCl}_2$  gave 55%  $\text{Et}_2\text{Ge(CH:CH}_2)_2$ , b.  $149.8^\circ$ , 1.4575, 1.0192. Similarly were prepd. undescribed:  $\text{Et}_2\text{Si(CH:CH}_2)_2$ ,  $\text{EtSi(CH:CH}_2)_3$ ,  $\text{MeSi(CH:CH}_2)_3$ ,  $\text{Me}_3\text{SiCH:CH}_2$ ,  $\text{EtGe(CH:CH}_2)_3$ ,  $\text{Et}_2\text{Si(CH:CH}_2)_2$ ,  $\text{PhMeSi(CH:CH}_2)_2$  and  $\text{PhSi(CH:CH}_2)_3$ . The tetrahydrofuran must be distd. from Na before use.

*organometallic*

New method of synthesis of organothallium compounds of class  $ArTlX_2$ .  
V.P.Glushkova and K.A.Kocheshkov (L.Ya.Karpov Phys.Chem.Inst.). Doklady  
Akad.Nauk S.S.S.R. 116, 233-5(1957).

Keeping equimolar mixture of  $(iso-PrCO_2)_3Tl$  and  $Ph_2Hg$  0.5 hr. in  $CHCl_3$  gave a ppt. of 87.9%  $(iso-PrCO_2)_2TlPh$ , m.221-2°; with 1:2 proportion of the reactants there formed similarly 80.9%  $iso-PrCO_2TlPh_2$ , m.241°. Heating  $(iso-PrCO_2)_3Tl$  and  $C_6H_6$  at 100° in sealed vessel 18 hrs. gave 90%  $(iso-PrCO_2)_2TlPh$ . Similarly  $(iso-PrCO_2)_3Tl$  and  $iso-PrCO_2TlPh_2$  gave overnight 100%  $(iso-PrCO_2)_2TlPh$ . The latter treated in MeOH with 15%  $NH_4OH$  gave a ppt. which suspended in MeOH and treated with 1.5N HCl in MeOH gave  $PhTlCl_2$ , m.233°. Reaction of  $(iso-PrCO_2)_3Tl$  with 1 mole  $(p-BrC_6H_4)_2Hg$  in warm  $CHCl_3$  gave 50%  $(iso-PrCO_2)_2TlC_6H_4Br-p$ , dec.219°, which with EtOH-HCl gave  $p-BrC_6H_4TlCl_2$ , m.261°.



*organ arsenic*  
G.V. Madoks (State Agric. Inst., Saratov). Doklady Akad. nauk S.S.S.R. 117, 993-5 (1957).

Mixing 0.68 g.  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in 96% EtOH with 1.44 g.  $\text{Ph}_3\text{AsCH}_2\text{PhNO}_3$  and heating on a steam bath gave on evapn. colorless plates of  $\text{La}(\text{NO}_3)_3 \cdot 2[\text{Ph}_3\text{AsCH}_2\text{Ph}]\text{NO}_3$ , m. 159.5° (from EtOH). Similarly formed  $\text{Ce}(\text{NO}_3)_3 \cdot 2[\text{Ph}_3\text{AsCH}_2\text{Ph}]\text{NO}_3$ , m. 163.75-64° (from EtOH), and  $\text{Pr}(\text{NO}_3)_3 \cdot 2[\text{Ph}_3\text{AsCH}_2\text{Ph}]\text{NO}_3$ , m. 165-5.25° (from EtOH), and  $\text{Nd}(\text{NO}_3)_3 \cdot 2[\text{Ph}_3\text{AsCH}_2\text{Ph}]\text{NO}_3$ , m. 166.25° (from EtOH). Ce salt is yellowish, Pr salt is yellow-greenish, and Nd salt is lilac in color. The Nd salt was least soluble, La was most soluble.

The nature of spontaneous change in viscosity of solutions of salvarsan. M.Ya.Kraft and E.N.Sytina (S.Ordshonikidze AllUnion Chem.Pharm.Res.Inst., Moscow). Doklady Akad.Nauk S.S.S.R. 116, 89-92(1957).

The work described below was done under  $\text{CO}_2$  to prevent oxidation. Salvarsan in the form of sulfate was made up as 1% soln. in N and 2N HCl and allowed to stand without contact with air for 3 days when a decided increase of its viscosity takes place. This treatment results in increase of the mol.wt. of about five fold, with evident formation of four new As-O-As bonds. Salvarsan isolated by pptn. of its alkaline soln. with HCl was subjected to a similar treatment and showed a very considerable increase of viscosity with apparent mol.wt. rising to  $10^6$  level. This on being kept in 2NHCl ~~fixes~~ decreased its viscosity after many days. The results indicate that the high polymer nature of salvarsan is due to inherently large molecule and not to mere assocn.

*in aluminum*

**Utilization of aluminumtrialkyls in synthesis of hetero-organic compounds.**

**L.I. Zakharkin and O.Yu. Oxhlobystin (Inst. Hetero-org. Compounds, Moscow).**

**Doklady Akad. Nauk S.S.S.R. 116, 236-8(1957).**

Addn. of 19 g.  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  to 27.1 g.  $\text{iso-Bu}_3\text{Al}$  at  $60-5^\circ$  gave 60%  $\text{iso-Bu}_3\text{B}$ ,  $b_{745} 174-6^\circ$ ,  $b_{57} 57-8^\circ$ ,  $n_D^{22.5} 1.4188$ . Passage of  $\text{BF}_3$  into  $\text{Et}_3\text{Al}$  in decalin gave  $\text{Et}_3\text{B}$ ,  $b_{95} 5-6^\circ$ . Reaction of  $\text{iso-Bu}_3\text{Al} \cdot \text{Et}_2\text{O}$  with  $\text{SbF}_3$  in  $\text{Et}_2\text{O}$  gave 77%  $\text{iso-Bu}_3\text{Sb}$ ,  $b_{810} 1.5^\circ$ ,  $n_D^{19.5} 1.4955$ ,  $d_{20} 1.124$ ; dibromide,  $m. 95^\circ$ .

Reaction of equimolar amounts of  $\text{iso-Bu}_3\text{Al}$  and  $\text{AsCl}_3$  in  $\text{Et}_2\text{O}$  gave not  $\text{R}_3\text{As}$  but mainly  $\text{iso-BuAsCl}_2$  and  $\text{iso-Bu}_2\text{AsCl}$ , the former,  $b_{857} 5-8^\circ$ ,  $n_D^{20.5} 1.5108$ ,  $d_{20} 1.4126$ , the latter  $b_{876} 7^\circ$ ,  $n_D^{20.5} 1.4862$ ,  $d_{20} 1.1265$ . Reaction of  $\text{iso-Bu}_3\text{Al}$  and  $\text{PCl}_3$  gave a vigorous formation of a complex with  $\text{AlCl}_3$  and from the reaction mixture there was distd. a low yield of  $\text{iso-BuPCl}_2$ ,  $b_{148} 8-9^\circ$ ,  $n_D^{20} 1.4818$ ,  $d_{20} 1.1268$ ; further heating of the residue gave severe decompn. and formation of free P. Equimolar amounts of  $\text{R}_3\text{Al}$  and  $\text{HgBr}_2$  or  $\text{HgCl}_2$  in  $\text{Et}_2\text{O}$  or hexane gave mainly  $\text{R}_2\text{Hg}$ ; thus were formed 65.5%  $\text{iso-Bu}_2\text{Hg}$ ,  $b_{651} 23-23.5^\circ$ ,  $n_D^{20} 1.4964$ ,  $d_{20} 1.770$ ;  $\text{iso-BuHgBr}$ ,  $m. 78^\circ$ ;  $\text{Et}_2\text{Hg}$  (58%).

Reaction of 18/8 g.  $\text{SnCl}_4$  and 19 g.  $\text{iso-Bu}_3\text{Al}$  in heptane at  $40-8^\circ$  gave after treatment with  $\text{NaOH}$  53.6%  $\text{iso-Bu}_4\text{Sn}$ ,  $b_{8128} 8-9^\circ$ ,  $n_D^{19.5} 1.4751$ ,  $d_{20} 1.0517$  and  $\text{iso-Bu}_3\text{SnOSnBu-iso}_3$ ,  $b_{12197} 7-8^\circ$ ,  $n_D^{21} 1.4850$ ,  $d_{20} 1.1547$ .

*Organosilicon Titanium* (5)

**Synthesis of tetrakis (trialkyl (aryl)siloxy)titanium by the method of transesterification of tetraalkoxy titanates.**

B.N. Dolgov and N.F. Orlov (Silicate Chem. Inst., Leningrad). Doklady Akad. Nauk S.S.S.R. 117, 617-8 (1957).

Heating equimolar mixture of  $(RO)_4Ti$   $R_x$  and  $R_3SiOH$  in the presence of 0.01% Na with slow distn. of ROH was used to prepare  $(R_3SiO)_4Ti$ . Thus 5 g.  $Ti(OEt)_4$ , 13 g.  $Me_3SiOH$  and 0.01 g. Na gave 50.5%  $(Me_3SiO)_4Ti$ ,  $b_{10} 110^\circ$ ,  $n_D^{20} 1.4275$ ,  $d_{20} 0.9004$ . Similarly were prepd.: 90.2%  $(MeEt_2SiO)_4Ti$ ,  $b_3 154^\circ$ , 1.4545, 0.9244; 98%  $(Et_3SiO)_4Ti$ ,  $b_{3.5} 195^\circ$ , m. 99-101°; 83%  $(MePr_2SiO)_4Ti$ ,  $b_3 186-8^\circ$ , 1.4570, 0.9044; 85%  $(Ph_3SiO)_4Ti$ , m. above 480°, was prepd. by refluxing the ingredients in  $C_6H_6$  6 hrs.

Synthesis of Approved For Release 2008/12/09 : CIA-RDP80T00246A003900030002-4 presence of tertiary amines.

B.N. Dolgov and N.F. Orlov (Silicate Chem. Inst., Leningrad). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1957, 1395-6.

To 28.5 g.  $\text{MeEt}_2\text{SiOH}$  in  $\text{C}_6\text{H}_6$  and 18.3 g. pyridine was added at  $0^\circ$  11.4 g.  $\text{TiCl}_4$  and after 1 hr. at  $70-80^\circ$  the filtered soln. gave 38.8%  $(\text{MeEt}_2\text{SiO})_4\text{Ti}$ ,  $b_6 186^\circ$ ,  $n_D^{20} 1.4565$ ,  $d_{20} 0.9248$ . Similarly were prepd.: 45.5%  $(\text{Et}_3\text{SiO})_4\text{Ti}$ ,  $b_7 227-30^\circ$ ,  $m. 95-7^\circ$  (with  $\text{PhNMe}_2$  acid acceptor the yield was 89.5%), and 96%  $(\text{Ph}_3\text{SiO})_4\text{Ti}$ ,  $m. \text{about } 480^\circ$  (from o-xylene).

*organosilcontitanium*

**Reaction of dialkoxytitanium oxides with tetraalkoxysilanes.**

A. I. Nosnitsyn and G. V. Nogina. Doklady Akad. Nauk S.S.S.R. 117, 249-51 (1957). Cf. this J. 95, 813 (1954).

While conventional cryoscopic method gives decidedly high values for observed mol. wts. of  $(RO)_2TiO$  owing to association, the isopiestic method showed that the Pr and the Bu members are substantially monomeric in up to 0.1% solns. in  $C_6H_6$ , which fact indicates the existence of a double bond between Ti and O. This was confirmed by addn. reactions below. To 5.5 g.  $(PrO)_2TiO$  in hexane was added 80 g.  $Si(OPr)_4$  and the mixture was refluxed in absence of moisture 4 hrs. yielding on distn. 29%  $(PrO)_3TiOSi(OPr)_3$ ,  $b_p 125-6^\circ$ ,  $b_{10 \times 10^{-6}} 66-9^\circ$ ,  $n_D^{20} 1.4647$ . Similarly 6.9 g.  $(PrO)_2TiO$  and 5 g.  $Si(OPr)_4$  gave 36%  $(PrO)_2Si(OTi(OPr)_3)_2$ ,  $b_p -578-81^\circ$ , 1.4910. Reaction of 0.2 g.  $(iso-BuO)_2TiO$  with 12.56 g.  $(iso-BuO)_4Si$  gave  $(iso-BuO)_3TiOSi(OBu-iso)_3$ ,  $b_p -575-8^\circ$ , 1.4610; distn. at 1 mm. led to decompn. which yielded  $(iso-BuO)_4Ti$ . The reaction also gave a substance, m.  $193-5^\circ$ , contg. 40.7-41% C and 8% H. Reaction of  $2(EtO)_2TiO$  with  $(EtO)_4Ti$  or that of  $(PrO)_2TiO$  with  $(PrO)_4Si$  gave crystalline products which corresponded to  $(EtO)_2Ti(OTi(OEt)_3)_2$  and  $(PrO)_3TiOTi(OPr)_3$ , resp.

*monosilicon* ⑥

**Preparation of compounds with silathiacarbon links.**

N.S. Nadezkin, A.V. Topchiev and L.S. Povarov. Doklady Akad. Nauk S.S.S.R. 117, 245-8 (1957).

To a soln. of 13.6 g. pyridine in 100 ml.  $\text{Et}_2\text{O}$  satd. with  $\text{H}_2\text{S}$  there was added 40 g.  $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{Br}$  in 50 ml.  $\text{Et}_2\text{O}$  and the mixture was refluxed 5 hrs. in a weak stream of  $\text{H}_2\text{S}$ , and filtered ~~and~~ after cooling. The filtrate yielded 36.4%  $\text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{SH}$ ,  $b_{14} 58-60^\circ$ ,  $d_{20} 0.8632$ ,  $n_D^{20} 1.4604$ , and 41.9%  $\text{S}(\text{SiMe}_2\text{CH}_2\text{SiMe}_3)_2$ ,  $b_{3.5} 117-8^\circ$ ,  $m. -98^\circ$ ,  $d_{20} 0.8774$ ,  $n_D^{20} 1.4777$ . Passage of  $\text{H}_2\text{S}$  30 min. into 20 g. pyridine in 150 ml. MePh, followed by addn. of 72 g.  $\text{Et}_3\text{SiCH}_2\text{SiEt}_2\text{Br}$  and refluxing 12 hrs. in stream of  $\text{H}_2\text{S}$  gave after filtration 80.3%  $\text{Et}_3\text{SiCH}_2\text{SiEt}_2\text{SH}$ ,  $b_{3.5} 113-4^\circ$ ,  $d_{20} 0.8989$ ,  $n_D^{20} 1.4852$ . This refluxed with equimolar <sup>amount</sup> of the analogous bromide in MePh in the presence of pyridine 16 hr. gave 32.4%  $(\text{Et}_3\text{SiCH}_2\text{SiEt}_2)_2\text{S}$ ,  $b_3 202-4^\circ$ ,  $m. -85^\circ$ ,  $d_{20} 0.9108$ ,  $n_D^{20} 1.4980$ .

**Comparative effectiveness of alloys of silicon with copper and nickel used in direct synthesis of vinylchlorosilanes.**

M.F.Shostakovskii, E.M.Savotskii, D.A.Koshkin and L.V.Musatova. (N.D. Zelinskii Inst.Org.Chem.Moscow). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim. Nauk 1957n 1493-5. Cf. this J.1954,174; 1956,1150.

For direct synthesis of vinylchlorosilanes an alloy of Si with 20% Ni is more effective than the comparable Si-Cu alloy. The Ni alloy at 420-50° converted  $\text{CH}_2\text{:CHCl}$  to a range of products containing 14.8%  $\text{CH}_2\text{:CHSiCl}_3$  and 3.8%  $(\text{CH}_2\text{:CH})_2\text{SiCl}_2$ . The latter is absent from the catalyzate from Cu alloy, while the former ~~gives~~ is formed in a similar yield. An alloy of 80% Si, 10% Cu and 10% Ni gave 11%  $\text{CH}_2\text{:CHSiCl}_3$ .



Catalytic phenylation of hydrogen containing alkylchlorosilanes with benzene  
G.N.Mal'nova, B.P.Mikheev, A.L.Klobanskii, S.A.Golubtsov and N.P.Filimonova  
Doklady Akad.Nauk S.S.S.R.117, 623-5(1957).

Phenylation of  $\text{MeSiHCl}_2$  and  $\text{EtSiHCl}_2$  with  $\text{C}_6\text{H}_6$  is conveniently done with  $\text{H}_3\text{BO}_3$  catalyst (1-2%), which affords formation of  $\text{PhSiCl}_3$  which cannot be satisfactorily fractionated from  $\text{MePhSiCl}_2$ . Use of 0.1%  $\text{H}_3\text{BO}_3$  almost completely eliminates the formation of  $\text{PhSiCl}_3$  and avoids this difficulty. The reactions are run in autoclaves at  $240^\circ$  (lower temps. give poor yields) at this temp. there is formed 13.6%  $\text{MePhSiCl}_2$ , while higher temps lead to difficultly separable mixtures. In large scale runs the yields reached 40% with 3-5 moles  $\text{C}_6\text{H}_6$  per mole of  $\text{MeSiHCl}_2$ . The gaseous products consist mainly of  $\text{H}_2$  with some 5-10% volatile hydrocarbons, Pure  $\text{MePhSiCl}_2$ ,  $b_{749} 203.1^\circ$ ,  $d_{20} 1.1778$ ,  $n_D^{20} 1.5188$ . Similar reaction with  $\text{EtSiHCl}_2$  at  $250^\circ$  gave  $\text{EtPhSiCl}_2$ ,  $b. 225.2^\circ$ , 1.1554, 1.5198. Cf. Brit. 646,466 (CA 45,5184).

Halogenation of aromatic silanes. V. Preparation and properties of chlorobenzyl- and chloro-p-tolyltrichlorosilanes containing atoms of chlorine in the aliphatic part of the radical.

G.V. Motsarev and A.Ya. Yakubovich. Zhur. Obshchei Khim. 27, 2786-90 (1957).

Cf. this J. 26, 2622 (1956), 27, 1318 (1957).

Passage of  $\text{Cl}_2$  at 20 ml./min. into 14.3 g.  $p\text{-MeC}_6\text{H}_4\text{SiCl}_3$  and 0.1%  $(\text{Me}_2\text{CCN})_2$   $\text{N}_2$  over 4.5 hrs. finally at  $130-40^\circ$  gave an adduct of 6.2 g. and on distn. yielded 90%  $p\text{-Cl}_3\text{CC}_6\text{H}_4\text{SiCl}_3$ ,  $b_{14} 162-3^\circ$ ,  $n_D 1.66-7^\circ$  (from  $\text{Me}_2\text{O}$ ). Smaller input of  $\text{Cl}_2$  similarly gave 85.7%  $p\text{-ClCH}_2\text{C}_6\text{H}_4\text{SiCl}_3$ ,  $b_{15} 142-4^\circ$ ,  $d_{20}^{20} 1.4078$ ,  $n_D^{20} 1.5480$ , or 83.4%  $p\text{-Cl}_2\text{CHC}_6\text{H}_4\text{SiCl}_3$ ,  $b_{15} 133-5^\circ$ , 1.4788, 1.5541. Oxidation of any of the 3 substances gave  $\text{H}_2\text{O}$ . Chlorination of  $\text{PhCH}_2\text{SiCl}_3$  as above at  $85-95^\circ$  gave 87%  $\text{PhCHClSiCl}_3$ ,  $b_{15} 140-2^\circ$ , 1.4239, 1.5466, or 90%  $\text{PhCCl}_2\text{SiCl}_3$ ,  $b_{15} 146-9^\circ$ , 1.4896, 1.5357. Oxidation with  $\text{HNO}_3$  gave  $\text{H}_2\text{O}$ .

**Possibility of catalytic dehydrogenation of silicohydrocarbons.**

B.N.Dolgov, G.V.Golodnikov and K.G.Golodova (A.A.Zhdanov State Univ., Leningrad). ~~XXXX~~ Doklady Akad.Nauk S.S.S.R.117,987-9(1957).

Passage of  $\text{BuSiMe}_3$  over a selected chrome catalyst at  $550-75^\circ$  gave 6.2-8.6%  $\text{MeCH}_2\text{CHCH}_2\text{SiMe}_3$ , along with  $\text{Me}_4\text{Si}$ ,  $\text{C}_3\text{H}_8$ ,  $\text{Me}_3\text{SiH}$  and  $\text{CH}_4$ . The unsatd.silane was not isolated in pure state and probably contained other isomers, including  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH:CH}_2$ , the latter being confirmed spectroscopically. The substance forms a rather stable dibromide,  $b_p 88-90^\circ$ ,  $d_{20} 1.3581$ ,  $n_D^{20} 1.4918$ .

*ganosilicon*  
**Tetraacyloxysilanes in organic synthesis. X. Comparative action of catalysts in the reaction of acylation of benzene and thiophene by tetraacyloxysilanes.** Yu.K.Yur'ev, Z.V.Belyakova and N.S.Zefirov (State Univ., Moscow). Zhur.Obshehei Khim.27, 3264-71(1957). Cf. this j.26,2353(1956).

Acylation of thiophene with  $(\text{AcO})_4\text{Si}$  can take place not only in the presence of  $\text{SnCl}_4$ , but also with  $\text{ZnCl}_2$ ,  $\text{BeCl}_2$ ,  $\text{BF}_3$  or  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  in 25.5-46.5% yields and with  $\text{TiCl}_4$  in 93.5% yield. Acylation of  $\text{C}_6\text{H}_6$  occurs similarly in the presence of  $\text{AlCl}_3$  or  $\text{FeCl}_3$ ;  $\text{ZnCl}_2$ ,  $\text{BeCl}_2$ ,  $\text{BF}_3$  or  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  are ineffective in this case. Either pure  $(\text{AcO})_4\text{Si}$  may be used, or its crude prepn. formed from  $\text{SiCl}_4$  and  $\text{AcOH}$ . Acylation of aromatic compounds by anhydrides of silicic and org. acids is discussed; it is believed to proceed through a complex of the anhydride with the catalyst, the complex having a carbonium ion at the site of the acyl carbonyl group.

*silicon*

Synthesis of organosilicon compounds. IV. Hydrolysis of dimethyldichlorosilane by methyl alcohol with formation of linear polysiloxanes and methyl chloride.

V.S. Fikhtengol'ts, A.L. Klebanskii and K.A. Rshendzinskaya. Zhur. Obshchei Khim. 27, 2984-9 (1957).

It was shown that linear polysiloxanes may be prepd. satisfactorily from  $\text{Me}_2\text{SiCl}_2$  and  $\text{MeOH}$ , with almost total recovery of  $\text{MeCl}$  being possible if 250-300% excess  $\text{MeOH}$  is used. The method may be used for polysiloxane resins and oils from byproducts of synthesis of  $\text{Me}_2\text{SiCl}_2$  and affords a recovery of  $\text{MeCl}$  which may be reused in the direct synthesis of silanes. Addn. of  $\text{Me}_2\text{SiCl}_2$  to some 250% excess  $\text{MeOH}$  in the cold, followed by heating on a steam bath afforded the desired reaction; with reaction time of about 1-1.5 hrs. a recovery of 99%  $\text{MeCl}$  is possible, but rapid reaction (1-2 min.) yields but 90%  $\text{MeCl}$ . Purity of  $\text{MeOH}$  is essential. The heating period of 15-17 hrs. is advised for complete reaction; added catalysts do not aid the reaction satisfactorily ( $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{H}_2\text{SO}_4$ ). For best results the components are mixed over 0.25-0.5 hr. at 15-20°, stirred 0.75-1 hr., then gradually heated to reflux and heated until  $\text{MeCl}$  loss ceases. The reaction probably proceeds through methoxy substituted polysiloxanes. The products are suitable for usual technical applications and can be transformed to rubbery polymers by usual means.

*Organosilicon*  
**Synthesis of some triphenylmethyl and triphenylethyl siloxanes.**

V.S.Chugunov (Silicate Chem.Inst., Leningrad). Invent.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1368-70. Cf. this j.1956,1056, and Zhur.Obachh.Khim. 27,494(1957).

Refluxing 27.6 g.  $\text{Ph}_3\text{SiOH}$  with 4 g. Na in  $\text{C}_6\text{H}_6$  4 hrs., sepn. of unreacted Na and addn. with ice cooling of 25 g.  $\text{MeSiCl}_2$  in  $\text{C}_6\text{H}_6$  gave after refluxing 2 hrs. 28.5 g.  $\text{Ph}_3\text{SiOSiMeCl}_2$ , b.368-72°,  $d_{20} 1.2060$ ,  $n_D^{20} 1.575$ . Similarly  $\text{MeSiHCl}_2$  gave 64.6%  $\text{Ph}_3\text{SiOSiMeHCl}$ , b.356-62°, 1.1182, 1.567. Reaction of 10.8 g.  $\text{Ph}_3\text{SiOH}$  with Na as above and treatment with 12 g.  $\text{MeSiHCl}_2$  in  $\text{C}_6\text{H}_6$  3 hrs. at reflux gave 42.5%  $(\text{Ph}_3\text{SiO})_2\text{SiMeH}$ , m.170-1°.  $\text{Ph}_3\text{SiONa}$  from 13.8 g. silanol and 6 g.  $\text{Me}_2\text{SiCl}_2$  gave 49.8%  $(\text{Ph}_3\text{SiO})_2\text{SiMe}_2$ , m.155-6°. Similarly  $\text{MeSiCl}_2$  gave 34.5%  $(\text{Ph}_3\text{SiO})_3\text{SiMe}$ , m.224-5°. Similarly were prepd.: 69.5%  $\text{Ph}_3\text{SiOSiEtCl}_2$ , b.370-6°, 1.1618, 1.572; 58.4%  $\text{Ph}_3\text{SiOSiEtHCl}$ , b.365-70°, 1.1132, 1.568; and 26%  $(\text{Ph}_3\text{SiO})_3\text{SiEt}$ , m.219-20°.

Photochlorination of ethyltrichlorosilane in liquid state. *silica*

E. I. Il'heev. Doklady Akad. Nauk S.S.S.R. 117, 821-2 (1957).

Photochlorination of  $\text{EtSiCl}_3$  as described earlier (this J. 103, 484 (1956)) at  $15-20^\circ$  under 150 watt incandescent lamp radiation was studied. With 0.75 mole  $\text{Cl}_2$  the product contains 20%  $\text{MeCHClSiCl}_3$  and 43%  $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$  with but 3% polychloro deriva.; at 1 mole utilized  $\text{Cl}_2$  the mixture contains 18.3%  $\text{MeCHClSiCl}_3$  and 34.5%  $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ , the latter remaining at this level with even 1.5 moles utilized  $\text{Cl}_2$ . Polychlorinated products rise in concn. appreciably only when over 1 mole  $\text{Cl}_2$  per mole of silane is used. The products isolated include:  $\text{MeCHClSiCl}_3$ , b.  $137^\circ$ ,  $d_{20} 1.3934$ ,  $n_D^{20} 1.4539$ ;  $\text{ClCH}_2\text{CH}_2\text{SiCl}_3$ , b.  $152^\circ$ , 1.4190, 1.4640;  $\text{ClCH}_2\text{CHClSiCl}_3$ , b.  $182^\circ$ , 1.5352, 1.4963;  $\text{Cl}_2\text{CHCH}_2\text{SiCl}_3$ , b.  $177.2^\circ$ , 1.5243, 1.4609, and  $\text{Cl}_3\text{CCH}_2\text{SiCl}_3$ , b. about  $200^\circ$ , 1.6149, 1.4690.

**Synthesis of organosilicon compounds. II. Comparative activity of various types of contact masses used for synthesis of methylchlorosilanes.**

V.S. Fikhtengel'ts and A.L. Klebanskii. Zhur. Obshchei Khim. 27, 2475-9 (1957). Cf. this j. 26, 2502 (1956).

Expts. with direct synthesis of methylchlorosilanes from  $\text{MeCl}$  showed that powd. Cu-Si alloy being used as the reactor filler begins to function at  $335^\circ$  and gives 44% conversion; briquettes of Si and Cu begin to operate at  $335^\circ$  and give 36% conversion; briquettes with chemically pptd. Cu begin to operate at  $300^\circ$  and give 39% conversion, while another specimen started operating at  $265^\circ$  and gave 43.5% conversion. The most complete transition of Cu into the intermetallic compound was attained in an alloy of Si with 20% Cu done under  $\text{N}_2$ , but this catalyst owing to low porosity was rather ineffective. Pressing of powdered components into pellets gave the least conversion to intermetallic compound even after heating to  $800^\circ$  in  $\text{N}_2$ . The best contact mass is the pressed briquette with chemically pptd. Cu as this form has a highly developed surface area. The compn. of the catalyzate changes in the course of the reaction, owing to the change of catalyst compn. Chemically active metallic tube fillers are effective in this reaction as they also aid in conducting the heat from the reaction zone of the exothermic reaction. Thus, porcelain filler gave 7.8%  $\text{MeSiHCl}_2$ , 7.2%  $\text{Me}_2\text{SiCl}$ , 29.4%  $\text{MeSiCl}_3$  and 51.2%  $\text{Me}_2\text{SiCl}_2$ ; for Mg these figures were 7.2, 5.4, 29.6 and 50.5; for Zn they were 6.1, 3.8, 26, 56.8; for brass they were 6.9, 4.8, 23.7 and 58.0%, resp. These were added to the usual contact mass.



**Preparation and properties of some alkylsilane deuterides.**

V.A.Ponomarenko, Yu.P.Egorov and G.Ya.Vzenkova (M.D.Zelinskii Inst.Org. Chem., Moscow). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1958, 54-8.

Reduction of appropriate chlorosilanes with  $\text{LiD}$  (cf. this j.1954,504) gave the following deuterium contg.silanes:  $\text{D}_3\text{SiCH}_2^{\text{O}1}$ , b. $30.5^\circ$ ,  $d_{20}0.9630$ ,  $n_D^{20}1.4160$  (Raman spectrum in  $\text{cm}^{-1}$ : not cited);  $\text{C}_6\text{H}_{13}\text{SiD}_3$ , b. $114^\circ$ , 0.7389, 1.4123 ( 202(2), 280(0), 366(0), 420(1), 600(0), 645(4), 668(3), 685(4), 730(1), 748(3), 800(1), 845(1), 952(1), 1070(8), 1110(4), 1184(5), 1240(0), 1307(5), 1410(1), 1442(4), 1450(4), 1549(10), 1571(5), 2156(2), 2857(7), 2895(10), 2920(2), 2938(6), 2965(5) );  $\text{D}_3\text{SiCH}_2\text{CH}_2\text{SiD}_3$ , b. $47^\circ$ , 0.7424, 1.4107 ( 170(2), 452(5), 591(1), 639(2), 684(5), 705(1), 762(4), 1020(1), 1115(1), 1252(6), 1417(2), 1552(10), 1575(4), 2155(2), 2895(7), 2910(2) );  $\text{Et}_2\text{SiD}_2$ , b. $55^\circ$ , 0.7005, 1.3916 (238(1), 310(2), 406(1), 504(3), 520(4), 568(4), 615(5), 640(5), 683(3), 707(4), 960(1), 975(4), 1017(4), 1112(2), 1235(5), 1416(3), 1467(4), 1542(10), 1553(3), 2130(2), 2875(9), 2895(10), 2910(3), 2936(4), 2960(5) ); and  $\text{Et}_3\text{SiD}$ , b. $107^\circ$ , 0.7372, 1.4117 (300(0), 540(4), 587(6), 606(1), 703(0), 750(1), 974(4), 1020(4), 1047(0), 1110(3), 1138(0), 1235(5), 1420(3), 1470(4), 1530(6), 2105(2), 2875(10), 2896(10), 2910(10), 2938(3), 2960(5)). The Si-D vibrations cover the band of 1530-1570  $\text{cm}^{-1}$ ; the refraction of Si-D link is 3.23 ml./mole.

*organosilicon*

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Reaction of catalytic hydrocondensation of trialkyl- and triarylsilanes with hydroxy, oxo and polyhydroxy organic compounds.

B.M.Dolgov, Yu.I.Khudobin and N.F.Kharitonov (Silicate Chem.Inst., Leningrad). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1958, 113-5.

Heating 293 g.  $\text{EtBu}_2\text{SiH}$  with 63 g. 1,3,5- $\text{C}_6\text{H}_3(\text{OH})_3$  and 0.5 g.  $\text{CoCl}_2$  7 hrs. at 145-65 $^\circ$  until loss of  $\text{H}_2$  is terminated gave 94% 1,3,5- $(\text{EtBu}_2\text{SiO})_3\text{C}_6\text{H}_3$ , b. $3283^\circ$ ,  $d_{20}0.9148$ ,  $n_D^{20}1.4769$ . Similarly tribromophenol,  $\text{EtBu}_2\text{SiH}$  and catalytic amount of  $\text{SnBr}_4$  in 3 hrs. at 210-40 $^\circ$  gave 96% 2,4,6- $\text{Br}_3\text{C}_6\text{H}_2\text{OSiBu}_2\text{Et}$ , b. $172.2^\circ$ ,  $d_{20}0.9261$ , 1.4784, 1.5458. Similarly were obtained: 86%  $\text{MeEt}_2\text{SiO}$

0.8060, 1.4125; 93%  $\text{EtBu}_2\text{SiOPh}$ ,  $b_{760}^{291.6^\circ}$ , 0.9074, 1.4830; 90%  $\text{EtBu}_2\text{SiO}-$   
 $\text{C}_6\text{H}_4\text{OMe-o}$ ,  $b_4^{170^\circ}$ , 0.9440, 1.4834; 90%  $\text{MeBu}_2\text{SiOC}_6\text{H}_3\text{Me}(\text{Pr})-3,4$ ,  $b_5^{152^\circ}$ ,  
 0.8924, 1.4800; 93% ethyldibutylsiloxyborneol,  $b_5^{185.5^\circ}$ , 0.8936, 1.4643;  
 $1-\text{C}_{10}\text{H}_7\text{OSiBu}_2\text{Et}$ ,  $b_9^{194^\circ}$ , 0.9659, 1.5330;  $2-\text{C}_{10}\text{H}_7\text{OSiBu}_2\text{Me}$ ,  $b_4^{183^\circ}$ , 0.9635,  
 1.5334;  $\text{Et}(\text{iso-Bu})_2\text{SiOC}_6\text{H}_4\text{Me-o}$ ,  $b_6^{140.5^\circ}$ , 0.9088, 1.4846;  $m\text{-MeC}_6\text{H}_4\text{OSiMe}-$   
 $(\text{CH}_2\text{CH}_2\text{CHMe}_2)_2$ ,  $b_{751.1}^{293.2^\circ}$ , 0.8876, 1.4740;  $p$ -isomer,  $b_{756.4}^{316.5^\circ}$ , 0.8938,  
 1.4773;  $o\text{-C}_6\text{H}_4(\text{OSiBu}_2\text{Et})_2$ ,  ~~$b_{722.1}^{281.0^\circ}$~~   $b_7^{255^\circ}$ , 0.9151, 1.4810;  $m$ -isomer,  
 $b_5^{211.5^\circ}$ , 0.9136, 1.4800;  $p$ -isomer,  $b_5^{221^\circ}$ , 0.9151, 1.4795; methylidibutyl-  
 silyl 2,4-(methylidibutylsiloxy)benzoate,  $b_{5.5}^{300^\circ}$ , 0.9420, 1.4788;  $p\text{-ClC}_6\text{H}_4\text{-}$   
 $\text{H}_4\text{OSiBu}_2$ ,  $b_3^{196^\circ}$ , 0.9688, 1.4892;  $p\text{-BrC}_6\text{H}_4\text{OSiBu}_2\text{Et}$ ,  $b_3^{194^\circ}$ , 1.1168, 1.5015;  
 the yields were above 90% in all cases. As catalysts one may use halides  
 of Ni, Co, Cr, Ge, Zn or Sn.

Some reactions of the amine group in triethylaminosilane.

K.A.Andrianov, S.A.Golubtsov and E.A.Semenova. Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1958, 47-53.

$\text{Et}_3\text{SiNH}_2$  and its N-alkyl derivs. react with  $\text{H}_2\text{O}$  yielding the NO derivs., while reaction with alcoh. results in alkoxy derivs. Aminosilanes are sufficiently stable thermally to withstand heating for considerable time.

Reaction of 21 g.  $\text{MeNH}_2$  with 44.5 g.  $\text{Et}_3\text{SiCl}$  in  $\text{Et}_2\text{O}$  gave 53.4%  $\text{Et}_3\text{SiNHMe}$ ,

~~XXXX~~  $b_{770}^{151-3^\circ}$ ,  $n_D^{20}$  1.4295,  $d_{20}$  0.8011. Similarly were prepd.:  $\text{Et}_3\text{SiNMe}_2$ ,  $b_{770}^{166-7^\circ}$ , 1.4325, 0.8044;  $\text{Et}_3\text{SiNHEt}$ ,  $b_{745}^{166-7^\circ}$ , 1.4300, 0.7995;  $\text{Et}_3\text{SiNMe}_2$ ,  $b_{755}^{199.5-201^\circ}$ , 1.4400, 0.8167;  $\text{Et}_3\text{SiNH}_2$ ,  $b_{751}^{137^\circ}$ , 1.4275, 0.7982.


Heating  $\text{Et}_3\text{SiNH}_2$  in  $\text{N}_2$  7 hrs. at reflux resulted in 92% recovery of the starting material; in 53 hrs. 86% was recovered and 8.9%  $(\text{Et}_3\text{Si})_2\text{NH}$ , b.  $235-46^\circ$ , was obtained.  $\text{Et}_3\text{SiNEt}_2$  in 25 hrs. reflux gave 83% recovery and formation of a small amount of material, b.  $200-16^\circ$ . Formation of 79-81%  $(\text{Et}_3\text{Si})_2\text{NH}$  is attained by reacting  $\text{Et}_3\text{SiNH}_2$  and  $\text{Et}_3\text{SiCl}$  16 hrs. at  $160-70^\circ$ .

To 20 g.  $\text{Et}_3\text{SiNH}_2$  in 25 ml.  $\text{Et}_2\text{O}$  was rapidly added 4.14 g.  $\text{H}_2\text{O}$  and after 1 hr. stirring there formed 81.4%  $\text{Et}_3\text{SiOH}$ ,  $b_{740}^{152-4^\circ}$ , 1.4335, 0.8631; similarly were obtained: 71%  $\text{Et}_3\text{SiOH}$  from  $\text{Et}_3\text{SiNHMe}$ , 84% from  $\text{Et}_3\text{SiNMe}_2$ , 70% from  $\text{Et}_3\text{SiNHEt}$ . Reaction of  $\text{H}_2\text{O}$  with  $\text{Et}_3\text{SiNEt}_2$  failed to occur under these conditions but in aq.  $\text{Me}_2\text{CO}$  in 2 hrs. 73%  $\text{Et}_3\text{SiOH}$  was formed. Similar addn. of 2.8 g. abs.  $\text{EtOH}$  to 4 g.  $\text{Et}_3\text{SiNH}_2$  resulted in vigorous reaction and formation after 3-4 hrs. of 80%  $\text{Et}_3\text{SiOEt}$ . Similarly were obtained:  $\text{Et}_3\text{SiOPr}$ ,  $b_{753}^{171.5-2^\circ}$ , 1.4210, 0.8183;  $\text{Et}_3\text{SiOCHMe}_2$ ,  $b_{762}^{157-8^\circ}$ , 1.4220, 0.8237;  $\text{Et}_3\text{SiOBu}$ ,  $b_{754}^{191-125^\circ}$ , 1.4225, 0.8184;  $\text{Et}_3\text{SiOCH}_2\text{CHMe}_2$ ,  $b_{756}^{182-3^\circ}$ , 1.4195, 0.8131;  $\text{Et}_3\text{SiOCH}_2\text{CH}_2\text{CHMe}_2$ ,  $b_{759}^{201-3^\circ}$ , 1.4240, 0.8187;  $\text{Et}_3\text{SiOC}_8\text{H}_{17}-n$ , b.  $115-6^\circ$ , 1.4355, 0.8263.

**Synthesis of organosilicon compounds. V. Preparation of polysiloxanes with mixed radicals.**

A.L.Klebanskii, V.S.Fokhtengel'ts and A.V.Karlin. Zhur.Obshehei Khim. 27, 3321-4(1957). Cf. this j.27,2984(1957).

Chlorination of  $\text{Me}_2\text{SiCl}_2$  under ultraviolet light at  $10-20^\circ$  with 0.95 to 1.25 moles  $\text{Cl}_2$  gave fairly pure  $\text{ClCH}_2\text{SiMeCl}_2$  and  $\text{CHCl}_2\text{SiMeCl}_2$ . The former treated with aq.StOH and heated 12-15 hrs. with 4-5% concd.  $\text{H}_2\text{SO}_4$  at  $150^\circ$  gave charred product. Hydrolysis of the dichloride with MeOH and polycondensation with 3%  $\text{H}_2\text{SO}_4$  4 hrs. at  $80-5^\circ$  gave very sticky products which were black and brittle after vulcanization. Polycondensation of the chlorinated products above alone or with added  $\text{Me}_2\text{SiCl}_2$  gave linear polysiloxanes containing chloromethyl groups, these polymers being more sol. in MeOH and  $\text{H}_2\text{O}$  than polymers with identical radicals in the chain. The presence of chlorinated Me groups in polysiloxanes worsens their mechanical properties but improves their cold resistance. Treatment of such mixed polysiloxanes with MeO and  $\text{CH}_2\text{Cl}$  groups, with hyposulfite soln. yielded material which gave tests for the SH group; no individual substances were isolated.



# Polymerization of unsaturated organosilicon compounds under pressure.

## IV. Mono- and disilanes.

V.V.Korshak, A.M.Polyakova, A.A.Sakharova, A.D.Petrov, V.F.Mironov, V.G. Glukhovtsev and G.I.Nikishin (Inst.Hetero-org.Compounds, Acad.Sci.,Moscow). Zhur.Obshchei Khim.27, 2445-9(1957). Cf. Doklady Akad.Nauk S.S.S.R.99,785 (1954), and this j.26,1209(1956).

It was shown that vinyl silanes which carry Et and MeO groups are more prone to polymerize than are their analogs with Me,Pr and other radicals. The allyl silanes are more readily polymerizable than are methallyl analogs. The monomers were heated under 6000 atm.pressure at 120° with up to 3% (Me<sub>3</sub>CO)<sub>2</sub> initiator. Polymers were formed from: Me<sub>3</sub>SiCH:CH<sub>2</sub>, Et<sub>3</sub>SiCH:CH<sub>2</sub>, Pr<sub>3</sub>SiCH:CH<sub>2</sub>, Bu<sub>3</sub>SiCH:CH<sub>2</sub>, Et<sub>3</sub>SiCH<sub>2</sub>CH:CH<sub>2</sub>, Me<sub>3</sub>SiCMe:CHMe, Me<sub>3</sub>SiCMe:CHCH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CN, Me<sub>3</sub>SiCMe:CHCH<sub>2</sub>OH, 1-C<sub>10</sub>H<sub>7</sub>Si(CH<sub>2</sub>CH:CH<sub>2</sub>)<sub>3</sub>, 1-C<sub>10</sub>H<sub>7</sub>Si(OCH<sub>2</sub>CH:CH<sub>2</sub>)<sub>3</sub>, (MeO)<sub>3</sub>SiCH:CHSi(OMe)<sub>3</sub>, (MeO)<sub>3</sub>SiCH:CHOl, (MeO)<sub>3</sub>SiOCl:CH<sub>2</sub>, (Me<sub>2</sub>)<sub>3</sub>SiCH<sub>2</sub>C(:CH<sub>2</sub>)-CH<sub>2</sub>Ol, CCl<sub>3</sub>Si(CH<sub>2</sub>CH:CH<sub>2</sub>)<sub>3</sub>, PrHSi(CH<sub>2</sub>CMe:CH<sub>2</sub>)<sub>2</sub>, iso-PrHSi(CH<sub>2</sub>CH:CH<sub>2</sub>)<sub>2</sub>, BuHSi(CH<sub>2</sub>CH:CH<sub>2</sub>)<sub>2</sub>, iso-BuHSi(CH<sub>2</sub>CH:CH<sub>2</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>4</sub>Si(CH<sub>2</sub>CH:CH<sub>2</sub>)<sub>2</sub>. Polymers were not formed from: EtMe<sub>2</sub>SiCH:CHMe<sub>2</sub>, EtMe<sub>2</sub>SiCH:CHMe, Me<sub>3</sub>SiCMe:CHMe at 1 atm. pressure, Me<sub>3</sub>SiCHMeCH:CHMe, Et<sub>3</sub>SiCMe:CHCH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CN, PrMe<sub>2</sub>SiCH:CHMe, Me<sub>3</sub>SiCPh:CH<sub>2</sub>, Me<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH, MeCH:C(SiMe<sub>3</sub>)<sub>2</sub>, Me<sub>3</sub>SiCH:CH<sub>2</sub>SiMe<sub>3</sub>, Me<sub>3</sub>SiCH<sub>2</sub>CH:CHCH<sub>2</sub>SiMe<sub>3</sub>, Et<sub>3</sub>SiOCH<sub>2</sub>CH:CH<sub>2</sub>SiEt<sub>3</sub>, and CCl<sub>3</sub>SiCH<sub>2</sub>CH:CH<sub>2</sub> (apparently a type error- ).

organosilicon polymers

# Reaction of some $\gamma$ -chloroalkylsilane chlorides with silicon under the conditions of direct synthesis.

A.D. Petrev, S.I. Sadykh-Zade, V.A. Penomarenko, B.A. Sokolov and Yu.P. Bgorev (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 27, 2479-86 (1957) Cf. Doklady Akad. Nauk SSSR 105, 496 (1955) and this j. 26, 1248 (1956).

$\gamma$ -Chloroalkyldichlorosilanes react with Si more readily than do their  $\alpha$ - and  $\beta$ -chloro analogs. The main reaction of the  $\alpha$ -isomers is not the formation of di and trisilane chlorides but rather dehydrochlorination to unsatd. silanes, accompanied by isomerization. Thus passage over usual 80-20 Si-Cu alloy of  $\text{MeSiCl}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$  at  $370-80^\circ$  gave 1.1%  $\text{MeSiHCl}_2$ , 2%  $\text{SiCl}_4$ , 14.1%  $\text{MeSiCl}_3$ , 23.5% mixed  $\text{MeSiCl}_2\text{CH}_2\text{CH}:\text{CH}_2$  and  $\text{MeSiCl}_2\text{CH}:\text{CHMe}$ , 7.1%  $\text{MeSiCl}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiHCl}_2$ , 14.1%  $\text{MeSiCl}_2(\text{CH}_2)_3\text{SiCl}_3$ , 3.8%  $(\text{MeSiCl}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2$ , and 3.5%  $(\text{MeSiCl}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{SiCl}_2$ , b.  $166-8^\circ$ , m.  $29-30^\circ$ . Similarly,  $\text{MeSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{Cl}$  gave 1%  $\text{HSiCl}_3$ , 7.6%  $\text{MeSiHCl}_2$ , 5.6%  $\text{SiCl}_4$ , 6%  $\text{MeSiCl}_3$ , 58%  $\text{MeSiCl}_2\text{C}_4\text{H}_7$  isomers, 5.2%  $\text{MeSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{SiHCl}_2$ , and 3.2%  $\text{MeSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{SiCl}_3$ .  $\text{EtSiCl}_2(\text{CH}_2)_3\text{Cl}$  gave 5.8%  $\text{EtSiCl}_3$ , 25.9% mixed  $\text{EtSiCl}_2\text{CH}_2\text{CH}:\text{CH}_2$  and  $\text{EtSiCl}_2\text{CH}:\text{CHMe}$ , 14.4%  $\text{EtSiCl}_2(\text{CH}_2)_3\text{SiHCl}_2$ , and 17%  $\text{EtSiCl}_2(\text{CH}_2)_3\text{SiCl}_3$ .  $\text{EtSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{Cl}$  gave 3.3%  $\text{HSiCl}_3$ , 1.2%  $\text{SiCl}_4$ , 12%  $\text{EtSiCl}_3$ , 49.4%  $\text{EtSiCl}_2\text{C}_4\text{H}_7$  isomers, 9.1%  $\text{EtSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{SiHCl}_2$ , and 10%  $\text{EtSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{SiCl}_3$ .  $\text{MeSiCl}_2(\text{CH}_2)_3\text{SiHCl}_2$ , b.  $206.5-7^\circ$ ,  $d_{20} 1.3450$ ,  $n_D^{20} 1.4625$ ;  $\text{EtSiCl}_2(\text{CH}_2)_3\text{SiHCl}_2$ , b.  $231-1.5^\circ$ , 1.2386, 1.4717;  $\text{EtSiCl}_2(\text{CH}_2)_3\text{SiCl}_3$ , b.  $241^\circ$ , 1.2960, 1.4728;  $\text{MeSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{SiHCl}_2$ , b.  $222^\circ$ , 1.2269, 1.4707;  $\text{EtSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{SiHCl}_2$ , b.  $235^\circ$ , 1.2100, 1.4735;  $\text{MeSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{SiCl}_3$ , b.  $234-5^\circ$ , -, -;  $\text{EtSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{SiCl}_3$ , b.  $245^\circ$ ;  $(\text{MeSiCl}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2$ , b.  $167-88.5^\circ$ , 1.2194, 1.4938;  $(\text{MeSiCl}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{SiCl}_2$ , b.  $166-8^\circ$ .

## Synthesis and transformations of oxygen containing organosilicon compounds. VI. Reaction of hydrogen containing alkyl(aryl)dichlorosilanes with organic alcohols.

M.P. Shostakovskii, D.A. Kechkin, V.L. Vinogradov and V.A. Neternan (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 27, 2487-91 (1957). Cf. Izvest. Akad. Nauk SSSR, otдел. khim. nauk 1956, 1269.

In equimolar mixture of alc. with alkylidichlorosilanes there are formed mainly  $\text{RSiH(OR)X}$ , at 1:2 ratio there form  $\text{RSiH(OR)}_2$ , while with larger proportions of alc. there are formed  $\text{RSi(OR)}_3$ . To 115 g.  $\text{MeSiHCl}_2$  was added at  $3-4^\circ$  46 g. EtOH (cooling to not over  $10^\circ$ ) the reaction becoming vigorous after initiation; after refluxing 0.5 hr. the mixture was kept overnight and distd. in  $\text{N}_2$  yielding 70.1%  $\text{MeSiHCl(OEt)}$ , b.  $100 34-8^\circ$ ,  $n_D^{20} 1.3851$ ,  $d_{20} 0.9188$ . With 92 g. EtOH there formed 40%  $\text{MeSiH(OEt)}_2$ , b.  $110 42^\circ$ , 1.3800, -. To 138 g. EtOH was added 115 g.  $\text{MeSiHCl}_2$  at  $10-15^\circ$  and after refluxing 5-6 hrs. there formed 63%  $\text{MeSi(OEt)}_3$ . Equimolar amounts of BuOH and  $\text{EtSiHCl}_2$

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mixed at 20° and heated 40 min. at 120° gave after standing overnight  
 85% EtSiHCl(OBu),  $b_{34.5}^{60}$ , 1.4126, 0.9285, and some EtSiH(OBu)<sub>2</sub>,  $b_{19.89}^{90.6}$ ,  
 1.4085, 0.8465. EtSiHCl<sub>2</sub> (129 g.) treated with 2 moles BuOH and  
 heated 2 hrs. at 120-30° gave after standing overnight 35% EtSiH(OBu)<sub>2</sub> and  
 14.4% EtSi(OBu)<sub>3</sub>. EtSiHCl<sub>2</sub> and 3 moles BuOH refluxed 12 hrs. gave 14.6%  
 EtSiH(OBu)<sub>2</sub> and 65% EtSi(OBu)<sub>3</sub>,  $b_{16}^{134}$ ,  $b_{17}^{135}$ , 1.4140, 0.8783. To 13 g.  
 Na in 300 g. BuOH was added 129 g. EtSiHCl<sub>2</sub>, gave after refluxing 12 hrs.  
 and filtration, 7.8% EtSiH(OBu)<sub>2</sub> and 83% EtSi(OBu)<sub>3</sub>.

Chemical industry and science in U.S.S.R.

N.M.Zhavoronkov. Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1277-83.

A brief historical review covering 1917-1957.

*organosilicon*

Reaction of telomerization and chemical transformations of telomers.

R.Kh.Freidlina (Inst.Hetero-org.Compounds, Acad.Sci.,Moscow). Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1333-43.

The previous work on telomerization by A.N.Nesmeyanov's group is reviewed with 29 references. It was shown that attempts to produce telomers by heating in stainless steel autoclave systems of  $\text{MeSiHCl}_2$ ,  $\text{EtSiHCl}_2$  or  $\text{Et}_3\text{SiH}$  with  $\text{C}_2\text{H}_4$  or  $\text{C}_3\text{H}_6$  in the presence of  $\text{Bz}_2\text{O}_2$ ,  $(\text{Me}_3\text{CO})_2$  or  $(\text{Me}_2\text{C}(\text{CN})\text{N})_2$  at 140-100° failed, but reactions of  $\text{C}_2\text{H}_4$  with  $\text{HSiCl}_3$ ,  $\text{MeSiHCl}_2$ ,  $\text{PhSiHCl}_2$  and  $\text{Et}_3\text{SiH}$ , and those of  $\text{C}_3\text{H}_6$  with  $\text{MeSiHCl}_2$  in stainless steel autoclave at 250-300° and 100-500 atm.pressure yielded without any added initiators a series of telomers of the above substances with up to 6 repeating units per molecule. The telomerization of  $\text{C}_2\text{H}_4$  with  $\text{MeSiHCl}_2$  gives 60-75% conversions in 5-10 min. at 325-50°; at 100 atm.pressure and 2:1 molar ratio of olefin to silane at 285° there occurs the best formation of higher telomers with over 3 repeating units, the yield of these reaching 23%. The reaction between  $\text{MeSiHCl}_2$  and  $\text{C}_2\text{H}_4$  at 50-70 atm. begins in the presence of a trace of  $\text{H}_2\text{PtCl}_6$  at room temp. and is exothermic, yielding  $\text{MeEtSiCl}_2$  in 100% yield. The amount of Pt deposited on vessel walls after 1 run suffices for several succeeding runs. Synthesis of amino carboxylic acids from tetrachlorealkanes is discussed at length (Cf.Nesmeyanov et al.,Chem.Techn. No.3,139(1957)), as are those of dicarboxylic acids. Mechanisms of radical rearrangements are discussed(Cf.Nesmeyanov et al. Doklady Akad.Nauk SSSR 113,828(1957). Cf. Uspekhi Khim.25,665(1956).



*Yakovlev*  
 Synthesis and transformation of vinyl compounds of silicon. 3. Preparation of vinylalkylchlorosilanes by reaction of acetylene with hydrogen containing chlorosilanes and study of some of their properties. M.F. Shostakovskii, D.A. Koshkin and V.L. Vinogradov (M.D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1957, 1452-6. Cf. this j. 1956, 1062.

Heating in autoclave 345 g.  $\text{MeSiHCl}_2$ , 1 g. Pd on  $\text{Al}_2\text{O}_3$  (0.5% Pd) and 60 l.  $\text{C}_2\text{H}_2$  2 hrs. at  $130-70^\circ$  gave 50%  $\text{CH}_2\text{:CHSiMeCl}_2$ ,  $b_{742}^{20} 91^\circ$ ,  $n_D^{20} 1.4270$ , 18 g.  $\text{CH}_2\text{:CHCH:CH}_2\text{SiMeCl}_2$ ,  $b_{11-11.5}^{20} 43-5.5^\circ$ ,  $n_D^{20} 1.444$ ,  $d_{20} 1.0917$ , 49.8 g.  $\text{Me}_2\text{Si}(\text{CH}_2\text{SiMeCl}_2)_2$ ,  $b_{772-5.5}^{20}$ ,  $n_D^{20} 1.4760$ ,  $d_{20} 1.2622$ , and 22.6 g.  $\text{MeSiCl}_2\text{CH}_2\text{CH}_2\text{CH:CHSiMeCl}_2$ ,  $b_{16}^{20} 95^\circ$ ,  $b_{16.5}^{20} 100^\circ$ ,  $n_D^{20} 1.4765$ ,  $d_{20} 1.1934$ , and 60 g. resinous matter. Similarly 344 g.  $\text{EtSiCl}_2\text{H}$ , 65.5 l.  $\text{C}_2\text{H}_2$  and 1.5 g. 0.5% Pd- $\text{Al}_2\text{O}_3$  gave 55%  $\text{CH}_2\text{:CHSiEtCl}_2$ ,  $b_{756}^{20} 118.5-9.5^\circ$ ,  $n_D^{20} 1.4323$ ,  $d_{20} 1.0664$ , 21 g.  $\text{EtSiCl}_2\text{CH:CHCH:CH}_2$ ,  $b_{4.5}^{20} 47^\circ$ ,  $b_{11}^{20} 62^\circ$ ,  $b_{11.5}^{20} 65^\circ$ ,  $n_D^{20} 1.4784$ ,  $d_{20} 1.0783$ , 35 g.  $(\text{CH}_2\text{SiEtCl}_2)_2$ ,  $b_{754}^{20} 249-50^\circ$ ,  $b_{101-2}^{20}$ ,  $n_D^{20} 1.4740$ ,  $d_{20} 1.187$ , 32 g.  $\text{EtSiCl}_2\text{CH}_2\text{CH}_2\text{CH:CHSiEtCl}_2$ ,  $b_{119-21}^{20}$ ,  $n_D^{20} 1.4669$ ,  $d_{20} 1.1910$  and 40 g. resins; with Pd-C catalyst the yield of  $\text{CH}_2\text{:CHSiEtCl}_2$  is 84%, the other products including  $\text{CH}_2\text{:CHCH:CH}_2\text{SiEtCl}_2$ ,  $(\text{CH}_2\text{SiEtCl}_2)_2$ , and I. The butadienyl deriv. on hydrogenation over Raney Ni gave  $\text{Et}_3\text{-iBu}$ .

Cyanoethylation of methyl- and ethyldichlorosilanes. *Yakovlev*

A.D. Petrov and V.M. Vdovin (M.D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1957, 1490-1.

Heating in autoclave 115 g.  $\text{MeSiHCl}_2$ , 60 g.  $\text{CH}_2\text{:CHCN}$  and 8 g. pyridine in 200 ml. MeCN at  $165^\circ$  6 hrs. gave a range of products including 12 g.  $\text{MeSiCl}_2\text{CH}_2\text{CH}_2\text{CN}$ ,  $b_{40}^{20} 111-5^\circ$ ,  $n_D^{20} 1.4518$ ,  $d_{20} 1.1722$ ; with  $\text{MeMgI}$  it gave  $\text{Me}_2\text{SiCH}_2\text{CH}_2\text{CN}$ ,  $b_{66}^{20} 88-92^\circ$ , 1.4240, 0.8309. Similarly  $\text{EtSiHCl}_2$  gave  $\text{EtSiCl}_2\text{CH}_2\text{CH}_2\text{CN}$ ,  $b_{40}^{20} 122-4^\circ$ , 1.4557, 1.1561. Reaction of acrylonitrile with  $\text{MeSiHCl}_2$  in MeCN with 0.5% Pt- $\text{SiO}_2$  at  $170^\circ$  gave a crystalline product,  $m.p. 51.5^\circ$ ,  $b_{16}^{20} 112^\circ$ .  $\text{SiHCl}_3$  and acrylonitrile in MeCN with pyridine gave 1.4557, 1.1561. Reaction of acrylonitrile with  $\text{EtSiHCl}_2$  in MeCN with 0.5% Pt- $\text{SiO}_2$  at  $170^\circ$  gave a crystalline product,  $m.p. 51.5^\circ$ ,  $b_{16}^{20} 112^\circ$ .

*Summary*  
Some transformations of organosilicon compounds with functional groups in  $\alpha$ - and  $\gamma$ -positions relative to the silicon atom.

V.F. Mironov and N.A. Pagenkina (N.D. Zelinskii Inst. Org. Chem., Moscow). Invest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1957, 1199-205.

Cf. Doklady Akad. Nauk SSSR 109, No. 2 (no pp. cited) (1956).

The  $\alpha$ -halide bond is more reactive than the  $\gamma$ -halide bond in reactions of halogen substituted silanes with nucleophilic reagents if the reaction is of bimolecular nature (reaction with  $\text{NaSCH}$ ). However since with  $\text{KOAc}$  the  $\gamma$ -position is more reactive, the mechanism of this replacement is evidently different. The  $\gamma$ -chlorides were prepd. by addn. of  $\text{RSiCl}_2$  to allyl or methallyl chlorides (cf. Doklady Akad. Nauk SSSR 106, 76 (1956)) as previously described but without  $\text{H}_2$  pressure; Pt on C is the best catalyst for the addn, as Pd on C or Raney Ni gave only  $\text{RSiCl}_2$ .  $\text{HSiCl}_2$  does not add to allyl chloride in presence of 2% Pt-C.  $\text{ClCH}_2\text{CHMeCH}_2\text{SiCl}_2\text{Me}$  and  $\text{MeMgCl}$  gave 78%  $\text{ClCH}_2\text{CHMeCH}_2\text{SiMe}_3$ ,  $b_{10} 50-3^\circ$ ,  $n_D^{20} 1.4380$ ,  $d_{20} 0.8812$ ; similarly  $\text{EtMgBr}$  gave 80%  $\text{ClCH}_2\text{CHMeCH}_2\text{SiEt}_2\text{Me}$ ,  $b_{10} 54-6^\circ$ ,  $1.4531$ ,  $0.9002$ ; however  $\text{PrMgBr}$  gave instead 48.7%  $(\text{ClCH}_2\text{CHMeCH}_2\text{SiMe})_2\text{O}$ ,  $b_{10} 150^\circ$ ,  $1.4612$ ,  $0.9762$ .  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiEtCl}_2$  and  $\text{MeMgCl}$  gave 76.5%  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SiEtMe}_2$ ,  $b_{10} 55-7^\circ$ ,  $1.4420$ ,  $0.8881$ . I refluxed 84 hrs. with  $\text{NaSCH}$  in  $\text{EtOH}$  gave 32.5%  $\text{Me}_3\text{SiCH}_2\text{CHMeCH}_2\text{SCH}$ ,  $b_{10} 100-1^\circ$ ,  $1.4710$ ,  $0.9239$ . Similarly was formed 76.7%  $\text{Et}_2\text{MeSiCH}_2\text{CH}_2\text{CH}_2\text{SCH}$ ,  $b_{10} 85-6^\circ$ ,  $1.4780$ ,  $0.9331$ , in 53 hrs. and 75%  $\text{Pr}_2\text{MeSiCH}_2\text{CH}_2\text{CH}_2\text{SCH}$ ,  $b_{10} 116-8^\circ$ ,  $1.4760$ ,  $0.9181$ , in 52 hrs.; 35.3%  $\text{Et}_2\text{MeSiCH}_2\text{CHMeCH}_2\text{SCH}$ ,  $b_{10} 82-7^\circ$ ,  $1.4801$ ,  $0.9320$ , in 83 hrs.  $\text{NaSCH}$  treated with a mixture of  $\text{Me}_3\text{SiCH}_2\text{Cl}$  and  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$  in  $\text{EtOH}$  and refluxed 16.5 hrs. gave 13 g. unreacted  $\gamma$ -chloride and 73.6%  $\text{Me}_3\text{SiCH}_2\text{SCH}$ ,  $b_{10} 46^\circ$ ,  $1.4680$ , -, with but a little  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SCH}$ ,  $b_{10} 70^\circ$ ,  $1.4690$ , -(13.5%). Heating  $\text{Me}_3\text{SiCH}_2\text{Cl}$  and  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$  with  $\text{AcOK}$  in  $\text{AcOH}$  in autoclave at  $200^\circ$  9 hrs. gave some unreacted chlorides and 33.4%  $\text{Me}_3\text{SiCH}_2\text{OAc}$  and 48%  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{OAc}$ ,  $b_{72} 182.5^\circ$ ,  $1.4218$ ,  $0.8743$ . Similarly was prepd. 34.5%  $\text{Me}_3\text{SiCH}_2\text{CHMeCH}_2\text{OAc}$ ,  $b_{12} 70-5^\circ$ ,  $1.4230$ ,  $0.8710$ . Refluxing  $\text{Me}_3\text{Si}(\text{CH}_2)_3\text{Cl}$  and  $\text{EtONa-EtOH}$  20 hrs. gave 71%  $\text{Me}_3\text{Si}(\text{CH}_2)_3\text{OEt}$ ,  $b_{10} 155-6^\circ$ ,  $1.4141$ ,  $0.7911$ ; a 73.5% yield was obtained by heating in autoclave 10 hrs. at  $160^\circ$  the above chloride with  $\text{KOH}$  in  $\text{EtOH}$ . The latter procedure at  $200^\circ$  gave 48.2%  $\text{Me}_3\text{SiCH}_2\text{CHMeCH}_2\text{OMe}$ ,  $b_{75} 150.5^\circ$ ,  $1.4178$ ,  $0.7972$ . Similar reaction of mixed  $\text{Me}_3\text{SiCHClMe}$  and  $\text{Me}_3\text{Si}(\text{CH}_2)_3\text{Cl}$  gave 49%  $\text{Me}_3\text{SiCH}(\text{CH}_3)_2$ ,  $b_{10} 54.5^\circ$ ,  $n_D^{20} 1.3852$ , and 60%  $\text{Me}_3\text{Si}(\text{CH}_2)_3\text{OMe}$ ,  $b_{76} 140^\circ$ ,  $1.4102$ ,  $0.7898$ . Passage of  $\text{Me}_3\text{Si}(\text{CH}_2)_3\text{OAc}$  through a glass tube at  $500^\circ$  gave 75.6% pure  $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ ,  $b_{10} 84-6^\circ$ ,  $1.4072$ ,  $0.7201$ . Similar pyrolysis of  $\text{MeSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{Cl}$  gave  $\text{MeSiCl}_2$ , unchanged chloride and 51% chlorides,  $b_{10} 345-50^\circ$ , which with  $\text{MeMgCl}$  gave 40.7% mixed  $\text{Me}_3\text{SiCH}_2\text{CHMeCH}_2$ ,  $\text{Me}_3\text{SiCH}=\text{CH}_2$ , and  $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CHMe}$ ,  $b_{742} 112-$

112.8°. Heating in autoclave 5 hrs. at 160°  $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$  with  $\text{Et}_3\text{NH}$  gave 56.7%  $\text{Me}_3\text{Si}(\text{CH}_2)_3\text{NEt}_3$ ,  $b_{756} 192.5^\circ$ , 1.4508, 0.7836; ethiodide, m. 125-7°.  $\text{Me}_3\text{SiCH}_2\text{CHMeCH}_2\text{OAc}$  kept 5 days in  $\text{NaOH}$  with a little  $\text{H}_2\text{SO}_4$  gave 76.5%  $\text{Me}_3\text{SiCH}_2\text{CHMeCH}_2\text{OH}$ ,  $b_{12} 73.5^\circ$ , 1.4534, 0.8331, which treated with a little  $\text{NaOH}$  and  $\text{CH}_3\text{CHO}$  gave in 1 day 79.5%  $\text{Me}_3\text{SiCH}_2\text{CHMeCH}_2\text{OCH}_2\text{CH}_2\text{OH}$ ,  $b_{1.5} 97^\circ$ , 1.4380, 0.8770, which kept in concd.  $\text{H}_2\text{SO}_4$  1 day at 0° and 1 day at room temp. gave on aq. treatment a yellowish solid, m. 130° (decomp.), which appeared to be  $\text{Me}_3\text{SiCH}_2\text{SOCH}_2\text{CH}_2\text{CH}_2\text{OH}$ .  $\text{MeSiCl}_2\text{CH}_2\text{CHMe}_2$ ,  $b_{725} 137.5^\circ$ , 1.4525, 1.0281.

*original*  
Reaction of addition of hydrosilanes to unsaturated compounds in the presence of platinized carbon.

A.D. Petrov, V.A. Ponomarenko, B.A. Sokolov and G.V. Odabashyan (N.D. Zelinskii Inst. Org. Chem., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1957, 1206-17.

The best yields of adduct are formed from  $\text{RSiHCl}_2$  and  $\text{R}_2\text{SiHCl}$ .  $\text{HSiCl}_3$  and  $\text{CH}_2\text{:CHCH}_2\text{Cl}$  with 1% Pt-C in 6 hrs. at 160° gave no adduct, but  $\text{MeSiHCl}_2$  gave 48%  $\text{MeSiCl}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ ,  $b_{754} 184.5^\circ$ ,  $d_{20} 1.2045$ ,  $n_D^{20} 1.4580$ , along with  $\text{MeSiCl}_3$  and  $\text{MePrSiCl}_2$ ; similarly  $\text{EtSiHCl}_2$  gave 48.6%  $\text{EtSiCl}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ ,  $b_{756} 206^\circ$ , 1.1809, 1.4661, along with  $\text{EtSiCl}_3$  and  $\text{EtPrSiCl}_2$ .  $\text{iso-PrSiHCl}_2$  gave 36%  $\text{iso-PrSiCl}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ ,  $b_{755} 55-6^\circ$ , 1.1512, 1.4685, while  $\text{tmm-BuSiHCl}_2$  gave 30%  $\text{tmm-BuSiCl}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ ,  $b_{774} 74^\circ$ , 1.1276, 1.4682.  $\text{MeEtSiHCl}$  gave 40.5%  $\text{MeEtSiClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ ,  $b_{759} 197.4^\circ$ , 1.0533, 1.4559, along with  $\text{MeEtSiCl}_2$  and  $\text{MeEtPrSiCl}$ ,  $b_{759} 141^\circ$ , 0.8825, 1.4246.  $\text{Et}_2\text{SiHCl}$  gave 21%  $\text{Et}_2\text{SiClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ ,  $b_{744} 218.5^\circ$ , 1.0331, 1.4614, along with  $\text{Et}_2\text{SiCl}_2$  and  $\text{Et}_2\text{PrSiCl}$ .  $\text{Et}_2\text{MeSiH}$  gave 1.8%  $\text{MeEt}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ ,  $b_{755} 55-6^\circ$ , 0.8937, 1.4432, along with  $\text{MeEt}_2\text{SiCl}$  and  $\text{Et}_2\text{MeSiH}$ . Similarly at 170°  $\text{HSiCl}_3$  and  $\text{CH}_2\text{:CHCH}_2\text{SiCl}_3$  gave 50%  $\text{CH}_2\text{-(CH}_2\text{SiCl}_3)_2$ ,  $b_{745} 228^\circ$ , 1.4394, 1.4732;  $\text{MeSiHCl}_2$  gave 64%  $\text{Cl}_2\text{Si}(\text{CH}_2)_3\text{SiMeCl}_2$ ,  $b_{741} 230^\circ$ , 1.3218, 1.4704;  $\text{Et}_2\text{SiHCl}$  gave 48.5%  $\text{Cl}_2\text{Si}(\text{CH}_2)_3\text{SiEt}_2\text{Cl}$ ,  $b_{741} 230^\circ$ .

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$9^\circ$ , 1.1758, 1.4680;  $\text{Et}_2\text{MeSiH}$  gave 33.8%  $\text{Cl}_2\text{Si}(\text{CH}_2)_2\text{SiMeEt}_2$ ,  $b_{749} 242^\circ$ , 1.0658, 1.4593. At  $160^\circ$   $\text{Cl}_2\text{C:CHCl}$  and  $\text{EtSiHCl}_2$  failed to give an adduct, but  $\text{CH}_2\text{:CHCl}$  and  $\text{MeSiHCl}_2$  gave 7.6%  $\text{MeSiCl}_2\text{CHClMe}$ .  $\text{MeSiHCl}_2$  and  $(\text{CF}_3)_2$  gave 14%  $\text{MeSiCl}_2\text{CF}_2\text{CHF}_2$  (cf. this J. 1956, 628), while  $\text{CF}_3\text{:CClF}$  gave 4.8%  $\text{MeSiCl}_2\text{SiCClFCHF}_2$ , along with  $\text{MeSiCl}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$ ,  $b_{755} 188^\circ$ , 1.5119, 1.3570. Cyclohexene and  $\text{MeSiHCl}_2$  at  $220^\circ$  gave 6%  $\text{C}_6\text{H}_{12}\text{SiCl}_2\text{Me}$ ,  $b_{752} 201^\circ$ , 1.0953, 1.4784. At  $170^\circ$   $\text{Me}_3\text{SiCH}_2\text{CH:CH}_2$  and  $\text{MeSiHCl}_2$  gave 54.5%  $\text{Me}_3\text{Si}(\text{CH}_2)_2\text{SiMeCl}_2$ ,  $b_{751} 201^\circ$ , 0.9730, 1.4428. At  $160^\circ$  butadiene and  $\text{MeSiHCl}_2$  gave some vinylcyclohexene and 14.9%  $\text{MeSiCl}_2\text{CH}_2\text{CH:CHMe}$ ,  $b_{750} 147^\circ$ , 1.0463, 1.4519, along with ~~2(3-cyclohexenyl)ethyl-methyldichlorosilane~~ 2(3-cyclohexenyl)ethyl-methyldichlorosilane,  $b_{779.5-80.5} 107^\circ$ , 1.0771, 1.4829. Butadiene and  $\text{EtSiHCl}_2$  at  $160^\circ$  gave 42.1%  $\text{EtSiCl}_2\text{CH}_2\text{CH:CHMe}$ ,  $b_{768} 171.5^\circ$ , 1.0450, 1.4566; this with  $\text{EtMgBr}$  gave  $\text{Et}_2\text{SiCH}_2\text{CH:CHMe}$ ,  $b_{749} 185.5-5^\circ$ , 0.7994, 1.4483, whose Raman spectrum was ( $\text{cm}^{-1}$ ): 173(1), 296(3), 333(1), 373(1), 401(1), 445(3), 505(0), 543(5), 580(2), 563(1), 739(1), 767(4), 795(2), 824(1), 909(3), 972(4), 1017(3), 1121(2), 1158(3), 1191(0), 1233(3), 1265(4), 1303(3), 1366(1), 1380(1), 1420(4), 1466(3), 1643(6), 1663(3), 2033(10), 2911(3), 2940(2), 2960(3), 2993(3). For comparison,  $\text{Cl}_2\text{SiCHMe:CH}_2$  and  $\text{EtMgBr}$  gave  $\text{Et}_2\text{SiCHMeCH:CH}_2$ ,  $b_{745} 187^\circ$ , 0.8090, 1.4518, whose Raman spectrum was: 174(1), 463(2), 515(4), 560(4), 746(2), 797(0), 889(3), 963(4), 1010(3), 1089(1), 1115(3), 1140(1), 1164(4), 1200(1), 1240(3), 1305(4), 1416(4), 1466(3), 1623(3), 2030(3), 2910(3), 2940(2), 2960(3), 3000(2), 3033(0). In the above addn. there also formed 2(3-cyclohexenyl)ethyl-ethyl-dichlorosilane,  $b_{7105} 105^\circ$ , 1.0612, 1.4845. At  $160^\circ$   $\text{MeSiHCl}_2$  and  $\text{CH}_2\text{:CHMeCH}_2\text{Cl}$  gave 56%  $\text{MeSiCl}_2\text{CH}_2\text{CHMeCH}_2\text{Cl}$  (cf. Doklady Akad. Nauk SSSR, 106, 76 (1956)).  $\text{EtSiHCl}_2$  and 3-cyclohexenylethane at  $180^\circ$  gave 75.9% ~~2(3-cyclohexenyl)ethyl-ethyl-dichlorosilane~~ 2(3-cyclohexenyl)ethyl-ethyl-dichlorosilane. Reaction of  $\text{MeSiHCl}_2$  with 1 mole  $\text{EtMgBr}$  gave 23.6%  $\text{MeEtSiHCl}$ ,  $b_{748} 67.5^\circ$ , 0.8830, 1.4035, some  $\text{MeEt}_2\text{SiH}$ ,  $b_{741} 77.5^\circ$ , and some  $\text{MeEtSiHBr}$ ,  $b_{741} 90^\circ$ , 1.2076, 1.4578. Similarly  $\text{EtMgBr}$  and  $\text{EtSiHCl}_2$  gave 32.8%  $\text{Et}_2\text{SiHCl}$ , some  $\text{Et}_2\text{SiH}$  and some 15%  $\text{Et}_2\text{SiHBr}$ ,  $b_{750} 121^\circ$ , 1.1903, 1.4472.

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Heating in  $\text{Et}_2\text{O}$   $\text{MeSiCl(CH}_2\text{CH}_2\text{CH}_2\text{Cl)}$  and  $\text{Mg}$  8 hrs. gave 18.8%  $\text{MeSi(CH}_2\text{)}_3$ ,  $b_{745}^{100^\circ}$ , 0.7965, 1.4388. Similarly was prepd. 8.8%  $\text{EtSiCl(CH}_2\text{)}_3$ ,  $b_{747}^{133.5^\circ}$ , 0.9791, 1.4570, from  $\text{EtSiCl(CH}_2\text{CH}_2\text{CH}_2\text{Cl)}$ . The use of  $\text{MeSiCl(CH}_2\text{CHMeCH}_2\text{Cl)}$  similarly gave 6.8%  $\text{MeSiCl(CH}_2\text{)}_3\text{CHMe}$ ,  $b_{740}^{115^\circ}$ , 0.9473, 1.4422.

**Reaction of alkylhalosilanes with trialkylsilanes.**

B.M.Dolgov, S.M.Borisov and M.G.Voronkov (State Univ., Leningrad). Zhur. Obshchei Khim. 27, 2692-7 (1957).

Reaction of  $R_3SiH$  with alkylhalosilanes in presence of  $AlCl_3$  affords a good synthesis of alkyl and dialkylsilanes;  $Et_2SiI_2$  failed to react with  $Et_3SiH$  under the conditions used. Distn. through a fractionating column of 20.9 g.  $Et_2SiBr_2$  and 19.8 g.  $Et_3SiH$  with 0.5 g.  $AlCl_3$  gave 59.2%  $Et_2SiH_2$ , b. 55.6°,  $n_D^{20}$  1.3916,  $d_{20}$  0.6657 and 89.4%  $Et_3SiBr$ , b. 164-6°, 1.4570, 1.1450. Similarly  $MePrSiCl_2$  and  $Et_3SiH$  gave 61.8%  $MePrSiH_2$ , b. 55.6°, 1.3857, 0.6756 and 97.8%  $Et_3SiCl$ , when small amount of  $AlCl_3$  was used, while with larger amount of the catalyst 47% iso- $PrMeSiH_2$  formed (b. 49.4°, 1.3790 and 0.6650), along with  $Et_3SiCl$ . Reaction of  $BuSiCl_3$  (24.6 g.), 48.5 g.  $Et_3SiH$  and 1.5 g.  $AlCl_3$  gave 98%  $BuSiH_3$ , b. 54.1°, 1.3912, 0.6756 and 95.9%  $Et_3SiCl$ . iso- $BuSiCl_3$  and  $Et_3SiCl$  gave 98.2% iso- $BuSiH_3$ , b. 49.5°, 1.3890, 0.6720, and 96.8%  $Et_3SiCl$ .  $MeEtCHSiCl_3$  and  $Et_3SiCl$  gave 97.5%  $MeEtCHSiH_3$ , b. 49.3°, 1.3898, 0.6756, and  $Et_3SiCl$ .  $BuSiCl_3$  and  $EtSiHCl_2$  failed to react in contact with  $AlCl_3$ . To 11.3 g.  $Et_2SiH_2$  and 0.5 g.  $AlCl_3$  was added 85 g.  $BuBr$  at 4°, yielding after 3 hrs. , finally at 35°, 93.5%  $Et_2SiBr_2$ , b. 166.5°, 1.4957, 1.5673. To 68 g.  $Et_2Si(OPh)_2$  and 5.4 g.  $Al$  was added 65.5 g.  $I_2$  and the mixture refluxed until violet color ~~was~~ vanished, gave 44.4%  $Et_2SiI_2$ , b. 221.2°, 1.5714, 1.9711.

*organosilicon*

Synthesis of organosilicon compounds. III. The reaction of direct synthesis of methylchlorosilanes.

A. A. Klebanskii and V. B. Fikhtengol'ts. Zhur. Obshchei Khim. 27, 2648-53 (1957). Cf. this j. 27, 2475 (1957), 26, 2502 (1956).

While over Si-Cu catalyst  $\text{MeCl}$  at  $280-300^\circ$  yields 5%  $\text{MeSiHCl}_2$ , 35%  $\text{Me}_2\text{SiCl}_2$  and 50%  $\text{Me}_2\text{SiCl}_2$ ,  $\text{EtCl}$  at  $190^\circ$  gives 51%  $\text{EtSiHCl}_2$ , 7%  $\text{Et}_2\text{SiCl}_2$  and 34%  $\text{Et}_2\text{SiCl}_2$ ,  $\text{CH}_2=\text{CHCl}$  at  $220^\circ$  gives 15%  $\text{HSiCl}_3$ , 45.5%  $\text{CH}_2=\text{CHSiHCl}_2$ , 25%  $\text{CH}_2=\text{CHSiCl}_3$  and 15%  $(\text{CH}_2=\text{CH})_2\text{SiCl}_2$ ,  $\text{PrCl}$  gives at  $170^\circ$  7%  $\text{HSiCl}_3$ , 82.5%  $\text{PrSiHCl}_2$  and 11%  $\text{Pr}_2\text{SiCl}_2$ ,  $\text{iso-PrCl}$  at  $150^\circ$  gives 34%  $\text{HSiCl}_3$  and 66%  $\text{iso-Pr-SiHCl}_2$ . Thus larger alkyl groups cease to yield the desirable  $\text{HSiCl}_3$  and  $\text{R}_2\text{SiCl}_2$  derivs, owing to lower thermal stability of the larger groups. While temp. rise in the reactor from  $350^\circ$  to  $400^\circ$  raises the conversion of  $\text{MeCl}$  the actual yield of  $\text{Me}_2\text{SiCl}_2$  declines from 35% to some 10%, with increased gaseous products of decompn. and increased content of  $\text{MeSiCl}_3$  in the catalyzate. With  $\text{EtCl}$ , the rise of temp. from  $190^\circ$  to  $250^\circ$  yields more  $\text{H}_2$  and  $\text{CH}_4$  with decreased yield of  $\text{Et}_2\text{SiCl}_2$  and relative increase of yield of  $\text{EtSiHCl}_2$ . While increased contact time raises the conversion of  $\text{MeCl}$  the actual rate of yield of condensate declines; ~~from 100% to~~ 5 sec. contact time gives <sup>20%</sup> ~~100%~~ conversion while 25 sec. contact gives 100% conversion, but yield of catalyzate drops from 25 to 12 g./hr. in the given installation; the compn. of catalyzate is almost unchanged. Thus the formation of  $\text{MeSiCl}_3$  and  $\text{Me}_2\text{SiCl}_2$  is not a consecutive reaction series. When  $\text{MeSiCl}_3$  was passed over Cu at  $350-400^\circ$  with or without  $\text{H}_2$ ,  $\text{HCl}$  or  $\text{MeCl}$ , no change was observed; the same was true of  $\text{Me}_2\text{SiCl}_2$ . Addn. of  $\text{MeSiCl}_3$  to  $\text{MeCl}$  in its passage over the catalyst actually lowered the yield of  $\text{MeSiCl}_3$ , while the yield of  $\text{Me}_2\text{SiCl}_2$  was unchanged. Increase of pressure to 4 atm. lowered the initiation temp. to  $260^\circ$  and raised the yield of  $\text{Me}_2\text{SiCl}_2$ , while the yield of  $\text{MeSiCl}_3$  declined somewhat. Such increased pressure along with longer contact lowers the yield of  $\text{Me}_2\text{SiCl}_2$  and raises that of  $\text{MeSiCl}_3$ . The best operating pressure is 4-5 atm.

# Reaction of chloroalkyl-alkyldichlorosilanes with aromatic compounds in the presence of aluminum chloride.

B.A. Chernyshev, M.B. Dolgaya and Yu.I. Agorov (Inst. Org. Chem., Acad. Sci., Moscow). Zhur. Obshchei Khim. 27, 2676-2681 (1957). Cf. 25, 2469 (1955).

Chloroalkyl-alkyldichlorosilanes can be used as alkylating agents in the Friedel-Crafts reaction. Refluxing 65.3 g.  $\text{ClCH}_2\text{SiMeCl}_2$ , 78 g.  $\text{C}_6\text{H}_6$  and 3 g.  $\text{AlCl}_3$  60 hrs., with addn. of 3.5 g.  $\text{AlCl}_3$  during that period, gave after addn. of 12 g.  $\text{FeCl}_3$  and 30 ml. iso-octane and heating 1 hr., a removable ppt. of  $\text{AlCl}_3 \cdot \text{FeCl}_3$ ; the filtrate gave 25.6%  $\text{PhCH}_2\text{SiMeCl}_2$ ,  $b_{740}^{20} 214-5^\circ$ ,  $n_D^{20} 1.5210$ ,  $d_{20} 1.636$ , and 8%  $\text{C}_6\text{H}_4(\text{CH}_2\text{SiMeCl}_2)_2$ ,  $b_{740}^{20} 299-302^\circ$ ,  $n_D^{20} 1.5365$ , 1.2765 (predominantly meta isomer, with both ortho and para being also present, as shown by Raman spectra).  $\text{MePh}$  similarly gave mixed isomers of  $\text{MeC}_6\text{H}_4\text{CH}_2\text{SiMeCl}_2$ , 15.8%,  $b_{754}^{20} 228-30^\circ$ , 1.5189, 1.1417. Reaction  $\text{MeCHClSiEtCl}_2$  with  $\text{C}_6\text{H}_6$  gave 49.8%  $\text{PhCH}_2\text{CH}_2\text{SiEtCl}_2$ ,  $b_{16}^{20} 130.2^\circ$ , 1.5150, 1.1122, while  $\text{PhCl}$  gave mixed isomers of  $\text{ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{SiEtCl}_2$ , 24.8%,  $b_{10}^{20} 147^\circ$ , 1.5238, 1.2095, and  $\text{MePh}$  gave mixed isomers of  $\text{MeC}_6\text{H}_4\text{SiEtCl}_2$ , 24.6%,  $b_{750}^{20} 269-70^\circ$ , 1.5132, 1.0941. Reaction of  $\text{ClCH}_2\text{CH}_2\text{SiEtCl}_2$  with  $\text{PhCl}$  gave isomers of  $\text{ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{SiEtCl}_2$ , 41.5%,  $b_3^{20} 135-9^\circ$ , 1.5267, 1.2109, while  $\text{MePh}$  gave 41.3% isomers of  $\text{MeC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{SiEtCl}_2$ ,  $b_3^{20} 121-5^\circ$ , 1.5152, 1.0967. Treatment of the appropriate dichloro derivs. above with  $\text{MeMgCl}$  gave: 82%  $\text{PhCH}_2\text{CH}_2\text{SiMe}_2\text{Et}$ ,  $b_{754}^{20} 226-7^\circ$ , 1.4924, 0.8724; 73%  $\text{ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Et}$ ,  $b_4^{20} 117-8^\circ$ , 1.5073, 0.9850; and 80%  $\text{MeC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Et}$ ,  $b_{15}^{20} 134-5^\circ$ , 1.4934, 0.8767. Addn. of  $\text{AlCl}_3$  to  $\text{ClCH}_2\text{CH}_2\text{SiEtCl}_2$  resulted in vigorous reaction which after 2 hrs. gave 95.3%  $\text{EtSiCl}_3$ . Similarly  $\text{MeCHClSiEtCl}_2$  gave 87.4%  $\text{EtSiCl}_3$ .  $(\text{MeC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{SiMe}_2)_2\text{O}$ ,  $b_4^{20} 211-3^\circ$ , 1.5078, 0.9455.

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**Synthesis of  $\beta$ -chloro and  $\beta,\beta$ -dichlorovinylalkyldichlorosilanes.**

A.B. Petrov, V.F. Mironov and D. Komanich (N.D. Zelinskii Inst. Org. Chem., Moscow). Invest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1957, 1393-4.

Cf. this j. 1956, 550.

Heating under 140 mm. vacuum a mixture of 511 g.  $\text{Cl}_2\text{CHCH}_2\text{SiCl}_3$  and 1 g.  $\text{AlCl}_3$ , 0.5 hr. resulted in rapid distn. of the contents; at 2/3 distn. the point of 2/3 distn. the residue was treated with 0.5 g.  $\text{AlCl}_3$  and distn. was continued; redistn. of the distillate gave 85%  $\text{ClCH:CHSiCl}_3$  (I), b. 133-4°. Passage of 412 g.  $\text{CCl}_2\text{:CHCl}$  and 160 g.  $\text{MeSiHCl}_2$  through a glass tube at 560° gave 27.8%  $\text{CCl}_2\text{:CHSiMeCl}_2$ , b. 75.2, 163.8°,  $n_D^{20}$  1.4893,  $d_{20}$  1.4056, along with  $\text{MeSiCl}_3$ ; at 600° the yield was 16%. Similar reaction with  $\text{EtSiHCl}_2$  gave 12% (at 520°)  $\text{CCl}_2\text{:CHSiEtCl}_2$ , b. 74.0, 187.2°, 1.4930, 1.3485. I and  $\text{EtOH}$  in  $\text{Et}_2\text{O}$  in presence of pyridine with cooling gave 56%  $\text{ClCH:CHSi(OEt)}_3$ , b. 76.5°, 1.4200, 1.0212. Similarly were obtained: 68.5%  $\text{CCl}_2\text{:CHSiEt(OEt)}_2$ , b. 71.8°, 1.4512, 1.0945 and 46%  $\text{CHCl:CHSiEt(OEt)}_2$ , b. 71.5°, 1.4305, 0.9936.  $\text{EtMgBr}$  from 120 g.  $\text{EtBr}$  treated with 49 g. I gave 73%  $\text{ClCH:CHSiEt}_3$ , b. 75.1, 191.5°, 1.4637, 0.9145. Similarly were obtained: 60%  $\text{CCl}_2\text{:CHSiMe}_3$ , b. 74.4, 143.3°, 1.4605, 1.0380; 40%  $\text{CCl}_2\text{:CHSiEtMe}_2$ , b. 32°, 1.4680, 1.0331; 60.5%  $\text{CCl}_2\text{:CHSiEt}_2\text{Me}$ , b. 60.5°, 1.4740, 1.0348; 56%  $\text{CCl}_2\text{:CHSiEt}_3$ , b. 3.5, 64°, 1.4786, 1.0368; and 32%  $\text{CHCl:CHSiEtCl}_2$ , b. 75.2, 162.8°, 1.4739, 1.2254. Cf. Agro, JACS 74, 3895 (1952).

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**Disproportionation of trialkylsilanes.**

S.M. Borisov, M.G. Voronkov and B.N. Dolgov (Silicate Chem. Inst., Leningrad). Invest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1957, 1396-8.

Refluxing 1.5 hrs. 28.2 g.  $\text{BuSiCl}_3$ , 45.2 g.  $\text{MeEt}_2\text{SiH}$  and 1 g.  $\text{AlCl}_3$  and subsequent distn. gave 6.4 g.  $\text{EtMe}_2\text{SiH}$ , b. 45.7°,  $n_D^{20}$  1.3783,  $d_{20}$  0.6681, 8.8 g.  $\text{BuSiH}_3$ , b. 54.1°, 1.3912, 0.6756, 8.4 g. mixed  $\text{MeEt}_2\text{SiH-EtMe}_2\text{SiCl}$ , 6.4 g.  $\text{MeEt}_2\text{SiCl}$  and 7.3 g. mixed  $\text{Et}_3\text{SiCl}$  and  $\text{BuSiCl}_3$ . Similarly 30.6 g.  $\text{MeEt}_2\text{SiH}$  and 1.5 g.  $\text{AlCl}_3$  in 3 hrs. gave 81.2%  $\text{EtMe}_2\text{SiH}$ , 4 g.  $\text{Et}_2\text{SiH}_2$ , b. 55.5°, 1.3911, 0.6820, and 7.7 g.  $\text{Et}_4\text{Si}$ .  $\text{Et}_3\text{SiH}$  and  $\text{AlCl}_3$  gave 58.2%  $\text{Et}_2\text{SiH}_2$  and 98%  $\text{Et}_4\text{Si}$ . Raman spectrum of  $\text{Et}_2\text{SiH}_2$ : 209(1), 245(2), 295(2), 322(1), 581(2), 606(10), 668(2), 702(2), 766(2), 941(5), 971(6), 1020(5), 1101(1), 1233(6), 1413(4), 1462(6), 2130(15), 2740(1), 2878(10), 2897(10), 2915(3), 2941(1), 2961(10). Thus the disproportionation of silanes is affected by conditions of the reaction and the amount of catalyst used.

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**Cleavage of organosiloxanes by halosilanes.**

**M.G. Voronkov and L.M. Chudoseva (Silicate Chem. Inst., Leningrad). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1957, 1415.**

It was shown that  $(R_3Si)_2O$  can be cleaved by  $R_3SiX$  in a reversible reaction. Reaction of  $Et_3SiCl$  with  $(Me_3Si)_2O$  or  $(MeEt_2Si)_2O$  gave, resp. 60-70%  $Me_3SiOSiEt_3$  and  $MeEt_2SiOSiEt_3$ . Similarly  $(Me_3Si)_2O$  and  $Et_3SiCl$  or  $Pr_3SiCl$  gave, resp., 54%  $(Et_3Si)_2O$ , 75%  $Me_3SiCl$  being formed, and 60%  $(Pr_3Si)_2O$  with 80%  $Me_3SiBr$ . Reaction of  $(Me_3Si)_2O$  with  $Me_2SiBr_2$ ,  $Et_3SiCl_2$  or  $Et_3SiHCl_2$  gave 15-75% corresponding trisiloxanes, affording a method for chain increase.